# Influence of calcium sulphate to plasticiser/superplasticiser interaction on concrete performance

By

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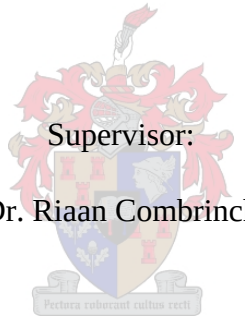
*Thesis present in fulfilment of the requirements for the degree of Master of Engineering (Research) in the faculty of Engineering at Stellenbosch University*

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# Abstract

With the continuously increasing use of concrete as a construction material the development of materials to enhance concrete performance has received a great deal of attention over the past few decades. However, one cause of inadequate concrete performance is found to stem from the cement production process itself. During the grinding of clinker, calcium sulphate dihydrate (gypsum) is added to produce cement. It is noted that the milling of clinker and calcium sulphate, to produce cement, causes peaks in temperature at localised areas within the mil. These increased temperatures result in the dehydration of calcium sulphate dihydrate to hemihydrate and to a lesser extent, anhydrite.

Calcium sulphate regulates the hydration of tricalcium aluminates; the reaction of tricalcium aluminates with calcium sulphate dominates the early hydration stage of cement. This facilitates a dormant period during which cementitious materials, such as concrete, maintain its workability which allows sufficient time for transport, placement and finishing of concrete. This dehydration of dihydrate to hemihydrate, and to a lesser extent anhydrite, influences the solubility and dissolution rate of the calcium sulphate in cementitious materials. The type of calcium sulphate therefore influences the hydration kinetics of cement. This dehydration of dihydrate to hemihydrate particularly influences the setting time and susceptibility to false/flash set of cementitious materials.

Modern concrete design often includes the use of chemical and mineral admixtures to provide improved fresh and hardened state properties that produce higher quality concrete structures. However, chemical admixtures such as plasticiser/superplasticiser, incorporated into concrete to increase workability or reduce water demand while maintaining workability, also have an affinity towards tricalcium aluminates in cement. This gives rise to cement – plasticiser/superplasticiser compatibility issues caused by the variation in type of calcium sulphate present in cement. This study therefore aims to establish the influence of the relation between calcium sulphate and plasticiser/superplasticiser on concrete performance.

The influence of this interaction on concrete performance is evaluated through the use of slump, slump flow, rheology, setting time and compressive strength properties. An attempt is made to explain the influence of the relation between calcium sulphate and plasticiser/superplasticiser on

the aforementioned concrete properties by considering the influence of plasticiser/superplastisers on calcium sulphate solubility. Solubility tests showed that the presence of plasticiser/superplasticiser increases the solubility of calcium sulphate hemihydrate and to a lesser extent, dihydrate. A correlation is found between the solubility of calcium sulphate and concrete fresh state properties. The presence of hemihydrate in cement is found to cause a decrease in concrete workability while increasing the rate at which concrete stiffens. The presence of hemihydrate also causes the rate of early compression strength gain to increase. This is verified by evaluating the influence of calcium sulphate – plasticiser/superplasticiser combinations on hydration temperature curves. From the evaluation of temperature hydration curves it is observed that the type of calcium sulphate present in cement influences the length of dormant period during hydration; hemihydrate causing a reduction of the dormant period. The magnitude of this reduction in length of dormant period is observed to be dependent on the presence and type of plasticiser/superplasticiser.

# Opsomming

Met die toeneemende gebruik van beton as konstruksiemateriaal, het die ontwikkeling van materiale om betonprestasie te verbeter baie aandag geniet oor die afgelope paar dekades. Daar bly steeds oorsake van onvoldoende betonprestasie wat oorsprong vind in byvoorbeeld die sementproduksieproses. Tydens die maal van klinker word kalsiumsulfaatdihidraat (gips) bygevoeg om sement te produseer. Temperatuurpieke kom voor op gelokaliseerde gebiede binne die meul tydens die maal van klinker en kalsiumsulfaat. Hierdie verhoogde temperature lei tot die dehidrasie van kalsiumsulfaatdihidraat tot kalsiumsulfaathemihidraat en tot 'n mindere mate, kalsiumsulfaatanhidriet.

Kalsiumsulfaat reguleer die hidrasie van trikalsiumaluminate in klinker. Dit is die reaksie van trikalsiumaluminate met kalsiumsulfaat wat die vroeë hidrasie periode van sement oorheers. Die reaksie gee aanleiding tot 'n dormante periode waartydens sementhoudende materiale, soos beton, genoegsame werkbaarheid behou wat die vervoer, plasing en afwerking van beton moontlik maak. Die dehidrasie van dihidraat tot hemihidraat, en tot 'n mindere mate anhidriet, beïnvloed die oplosbaarheid en diffusietempo van kalsiumsulfaat in sementhoudende materiale. Die tipe kalsiumsulfaat beïnvloed dus die hidrasie-kinetika van sement. Hierdie dehidrasie van dihidraat tot hemihydraat beïnvloed veral die settyd en moontlike vals/blits set van sementhoudende materiale.

Moderne betonontwerp sluit dikwels die gebruik van chemiese en mineraal bymiddels in om verbeterde vars en geharde eienskappe te lewer wat betonstrukture van hoër gehalte lewer. Chemiese bymiddels soos plastiseerders/superplastiseerders, wat by beton gevoeg word om die vars toestand te manipuleer, het egter ook 'n affiniteit vir trikalsiumaluminate in sement. Dit gee aanleiding tot probleme met die verenigbaarheid van sement - plastiseerder/superplastiseerder wat veroorsaak word deur die variasie in tipe kalsiumsulfaat wat in sement voorkom. Die doel van hierdie studie is om die invloed van die verband tussen kalsiumsulfaat en plastiseerder/superplastiseerder op betonprestasie, vas te stel.

Die invloed van hierdie interaksie op betongedrag word geëvalueer aan die hand van uitsakking, uitsakkingsvloei, reologie, settyd en druksterkte-eienskappe. Daar word gepoog om die invloed van die interaksie tussen kalsiumsulfaat en plastiseerder/superplastiseerder op die bogenoemde

beton-eienskappe te verklaar deur die invloed van plastiseerders/superplastiseerders op die oplosbaarheid van kalsiumsulfaat in ag te neem. Oplosbaarheidstoetse het getoon dat die teenwoordigheid van plastiseerder/superplastiseerder die oplosbaarheid van kalsiumsulfaathemihidraat en tot 'n mindere mate -dihidraat verhoog. ‘n Korrelasie is gevind tussen die oplosbaarheid van kalsiumsulfaat en die vars toestand eienskappe van beton. Daar is gevind dat die teenwoordigheid van hemihidraat in sement 'n afname in die werkbaarheid van beton veroorsaak, terwyl die tempo waarteen beton verstyf, verhoog word. Die teenwoordigheid van hemihidraat veroorsaak ook dat die tempo waarteen vroeë druksterkte toeneem, verhoog. Dit word bevestig deur die invloed van kalsiumsulfaat-plastiseerder/superplastiseerder kombinasies op hidrasie temperatuur te evalueer. Uit die evaluering van hidrasie temperatuurkurwes is daar gevind dat die tipe kalsiumsulfaat wat in sement teenwoordig is, die duurte van die dormante periode tydens hidrasie beïnvloed. Daar is gevind dat hemihidraat die dormante periode verkort, waar die grootte van hierdie verkorting afhanklik is van die teenwoordigheid en tipe plastiseerder/superplastiseerder.

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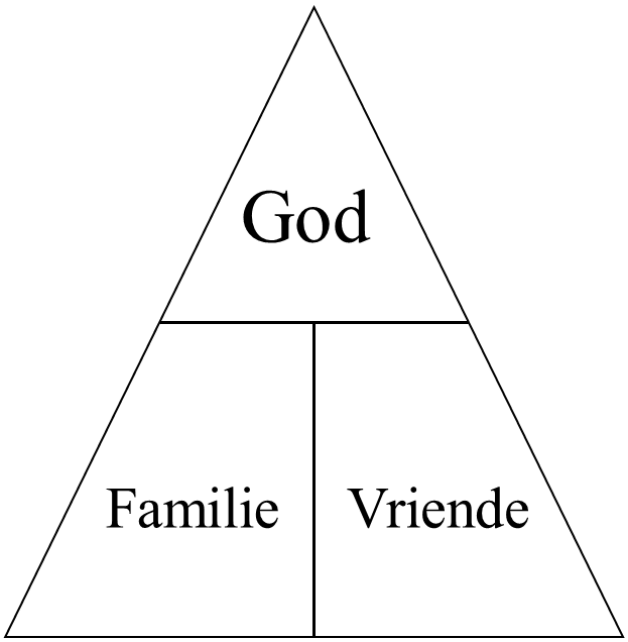


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# Chapter 1: Introduction

Cement production is a complex process that has been industrialised to produce large quantities of this structural material. Cement production consists of the mining of limestone and shale which are milled and blended in controlled ratios to produce a mixture consisting predominantly of silica and calcium carbonate. Although other materials may be added in small quantities, this mixture of limestone and shale form the foundation of cement production. This mixture is heated in a two stage process to between 1400 – 1500℃ in a kiln. Heating prompts the decarbonation of the mixture after which oxides combine to form a mixture referred to as clinker consisting predominantly of calcium silicates. However, the raw materials contain various other components, one being alumina oxides that produce calcium aluminates and – aluminoferrites during the heating process. The two aforementioned components form in small quantities within clinker but cannot be avoided and play an important part in cement hydration. Clinker exits the kiln at roughly 1200 degrees Celsius and is cooled to roughly 60 degrees Celsius before small quantities of calcium sulphate in the form of dihydrate, commonly known as gypsum, is added to the clinker to regulate the hydration of calcium aluminates and – aluminoferrites. The clinker – gypsum mixture is then milled to an average particle size of 45 µm to produce Portland cement. This grinding process, although being water or air cooled, causes an increase in temperature that results in partial dehydration of dihydrate (Domone and Illston, 2010). Research has shown that variations in the rheology, setting rate and strength of cement are often caused by variable milling temperatures (Bensted, 1982) (Gunay *et al.*, 2011).

This is because of the temperature sensitivity of calcium sulphate, the abovementioned mineral used in the production of cement. The elevated temperatures, produced during the milling of clinker and calcium sulphate dihydrate to produce cement, change the chemical properties of calcium sulphate. As calcium sulphate dihydrate dehydrates to hemihydrate the rate of reaction between calcium sulphate and the aluminate phase in cement is altered during cement hydration (Suzakawa and Kobayashi, 1966). It is therefore necessary to control the type of calcium sulphate present in cement as it effects the initial hydration of cementitious materials which is responsible for the initial structuration of cementitious materials i.e. loss of workability.

The development of concrete construction, through improved productivity, has been a priority for the past few decades. The development of concrete with high fluidity, such as self compacting

concrete (SCC), has played a key role in improving the productivity during construction due to its ability to compact with little to no vibration, without segregation. Highly flowable concrete mixes have been made possible with the development of chemical admixtures such as plasticisers and superplasticisers. It is for this reason that the development of plasticisers and superplasticiser are considered to be one of the most important developments in concrete technology, the difference between plasticisers and superplasticisers being their efficiency in inducing fluidity through water demand reduction (Alsadey, 2012).

However, the use of plasticiser/superplasticiser in concrete mix design emphasises the problem of variable grinding temperatures as both plasticiser/superplasticiser and calcium sulphate has an affinity towards the aluminate phase in cement. Furthermore, plasticiser/superplasticiser influence both the solubility and diffusion of dissolved calcium sulphate throughout the mix, preventing the dissolved sulphates from reaching the aluminate phase (Prince, Espagne and Aïtcin, 2003). This could result in the false set of cementitious materials if the concentration of dissolved calcium sulphate in the concrete solution is too high or flash set due to the unregulated hydration of aluminates.

Incompatible calcium sulphate to plasticiser/superplasticiser combinations can thus result in unexpected and unwanted workability (i.e. concrete rheology), setting time and strength development. The unexpected fresh state behaviour caused by compatibility issues upsets construction productivity as improper consolidation, finishing, texturing and curing can occur as a result thereof. These problems can also cause problems in the hardened state as rapid stiffening could lead to honey combing or increased voids. Furthermore, delayed setting times may lead to delayed strength gain. To ensure a mix design that results in adequate performance it is key to understand the interaction between calcium sulphate and plasticiser/superplasticiser and the effect of this interaction on the fresh state properties and hydration of cement. This study aims to improve upon the current understanding of the interaction between plasticiser/superplasticiser and calcium sulphate and the influence thereof on concrete performance.

If the influence of the calcium sulphate to plasticiser/superplasticiser interaction on concrete performance is known, proper combinations can be used to control the fresh state properties and initial structuration of concrete.

## 1.1 Problem statement

Plasticisers/superplasticiser are used more frequently in concrete production to ease construction. However, both plasticiser/superplasticiser and calcium sulphate have an affinity towards tricalcium aluminates that dominates the initial structuration of cementitious materials. To ensure a mix design that results in adequate performance it is key to understand the interaction between different types of calcium sulphate and plasticiser/superplasticiser and the effect of this interaction on the fresh state properties and hydration of cement.

## 1.2 Study objectives

This study aims to:

- Investigating the influence that the type of calcium sulphate, present in cement, has on the fresh state properties, initial structuration and hardened state strength development of concrete.
- Investigating the influence plasticiser/superplasticiser has on the fresh state properties, initial structuration and hardened state strength development of concrete.
- Identifying the influence of the combination of calcium sulphate and plasticiser/superplasticiser on the fresh state properties, initial structuration and hardened state strength development of concrete.

In summary the study aims to quantify the influence of the interaction between calcium sulphate and plasticisers/superplasticisers on the fresh state properties and hydration of cement.

## 1.3 Research significance

This study will assist in identifying potential cement – plasticiser/superplasticiser incompatibilities caused by the improper dihydrate or hemihydrate quantities in cement. Identifying these incompatibilities will assist in the design of concrete mixes that deliver project-adequate fresh and hardened state properties. This will result in improved industry productivity and infrastructure quality as concrete with adequate workability that allows for proper consolidation, finishing, texturing and curing is provided. With controlled fresh state properties, factors that influence hardened state properties, such as segregation caused honeycombing, can be eliminated.

Eliminating unexpected concrete behaviour will lead to more industry profit and less wastage which support the global drive towards a more sustainable built-environment.

## 1.4 Report Layout

Chapter 2 provides an overview on the hydration kinetics, leading to the structuration of concrete over time. The concept of rheology is discussed with emphasis placed on rheological parameters such as yield stress and plastic viscosity. The concept of thixotropy in cementitious materials are discussed, supplemented by an explanation on how thixotropy influences the rheology of concrete over time. Some of the rheological tests used to quantify the rheology of yield stress fluids i.e. cementitious materials, are discussed. Finally, relevant literature regarding the influence of various plasticisers/superplasticisers and types of calcium sulphate present in cement, as well as the influence of the relation between these additives, on the rheology of concrete, is presented to understand the occurrence of compatibility issues.

Chapter 3 lays out the test programme developed to quantify the influence of calcium sulphate to plasticiser/superplasticiser interaction on the fresh state properties and hydration of concrete. The properties of materials used and insight on the mix design process is provided. Finally, the tests performed are discussed in detail with emphasis placed on the test methodologies and parameters obtained from each test.

Chapter 4 provides a detailed discussion of the results obtained from the study. These results quantify the influence of calcium sulphate to plasticiser/superplasticiser interaction on the overall performance of concrete. The influence of this interaction on the fresh state properties are linked to practical aspects such as segregation resistance, formwork pressure, surface finish quality and pumping pressure. The influence of calcium sulphate to plasticiser/superplasticiser interaction on hydration is discussed and the influence thereof on the strength gain of concrete is provided.

Chapter 5 provides the conclusions drawn from the study on the influence of the relation between calcium sulphate and plasticiser/superplasticiser on concrete performance. The influence of this interaction on the fresh and hardened state properties as well as hydration of concrete is provided.

Chapter 6 lists recommendations that could be considered for future work, to further the understanding of calcium sulphate to plasticiser/superplastisers interaction.

# Chapter 2: Literature review

In this chapter an overview on the hydration kinetics, leading to the structuration of concrete over time, is provided. The concept of rheology is discussed with emphasis placed on rheological parameters such as yield stress and plastic viscosity along with the models commonly used to determine these parameters. The concept of thixotropy in cementitious materials are discussed, supplemented by an explanation on how thixotropy influences the rheology of concrete over time. Some of the rheological tests used to quantify the rheology of yield stress fluids i.e. cementitious materials, are discussed. Finally relevant literature regarding the influence of various plasticisers/superplasticisers and types of calcium sulphate present in cement, as well as the influence of the relation between these additives, on the rheology of concrete, is presented to understand the occurrence of compatibility issues.

## 2.1 Cement and concrete

Concrete is one of the most used man-made materials on Earth and is essential for societal development, forming a large source of employment. The production of cement therefore contributes to both society and the economy. Concrete has been produced for more than 200 years because of its durable and dependable nature. Furthermore, concrete is considered to be an affordable material with flexibility in design and plays a key role in increased urbanization and industrialization. Portland cement remains the most important constituent in concrete production today (Naik, 2008).

Currently cement is manufactured on an enormous scale and is a basic necessity for housing and other infrastructure. Cement consists out of various raw materials that are extracted from clayey schist, chalk and limestone rock. From these raw materials a fine powder is produced, referred to as raw meal. The raw meal is then heated to 1500 degrees Celsius after which it is rapidly cooled. At this stage the produced product is called clinker and forms the base of all cement production. The clinker is then mixed with dihydrate, commonly known as gypsum, to regulate the set time of the cement after which the mixture is milled to a fine powder referred to as ordinary Portland cement (OPC). Other minerals are often also added to the OPC, depending on the properties required, and bagged (Domone and Illston, 2010).

Modern concrete is engineered through the addition of supplementary cementitious materials (SCM) and admixtures to obtain certain properties. Ultra High Strength Concrete (UHSC) is designed to minimise cross sections and reduce the volume of concrete needed for a structure while maintaining durability. Self-compacting concrete (SCC) is developed to improve workability and ease construction. Foamed concrete is engineered as a light weight alternative to be used for heat insulation. Steps are also being taken to produce concrete that is more environmentally friendly by including waste material in the mix design, seeing that for each ton of cement produced a ton of $CO_2$ is released into the environment (National Ready Mixed Concrete Association, 2012). The advancements in the field of concrete are ongoing.

In South Africa the demand for housing is at an increase with more than 2.2 million low income housing units still in demand. The current construction methods and building materials available are sluggish and cost intensive making it difficult for South Africa to catch up to this growing demand. As a result research is currently undertaken to enrich the scope of building materials available that will lead to the reduction in life cycle cost and delivery time of infrastructure while promoting environmental protection. Currently researchers predominantly focus on partial cement replacement and the interaction between cement constituents to eliminate compatibility issues. This will result in cement that is cheaper, more environmentally friendly and improves construction productivity (Mapiravana, 2012).

### 2.1.1 Hydration process

The hydration process within cementitious materials start instantaneously with the addition of water, even though it seems that the cement paste or concrete might initially maintain its fluidity. It is only after approximately 1-2 hours that a loss in fluidity is noticed after the ‘initial set’ time. During the initial set period the mix does not gain any significant mechanical strength and no hardening takes place. Concrete will gain strength and harden over a period of days for as long as a few months; the rate of strength increase, decreasing with time. The time available for placement and handling of concrete is limited by the initial set whereas the ‘final set’ provides an indication of when strength gain and hardening commences. The hydration process is exothermic and therefore the heat emitted is often used to determine the rate at which reactions take place. Figure 2.1 depicts the heat emitted over time i.e. the rate of hydration within a cementitious material.

Using Figure 2.1, four phases of hydration can be identified (Domone and Illston, 2010; Scrivener *et al.*, 2019).

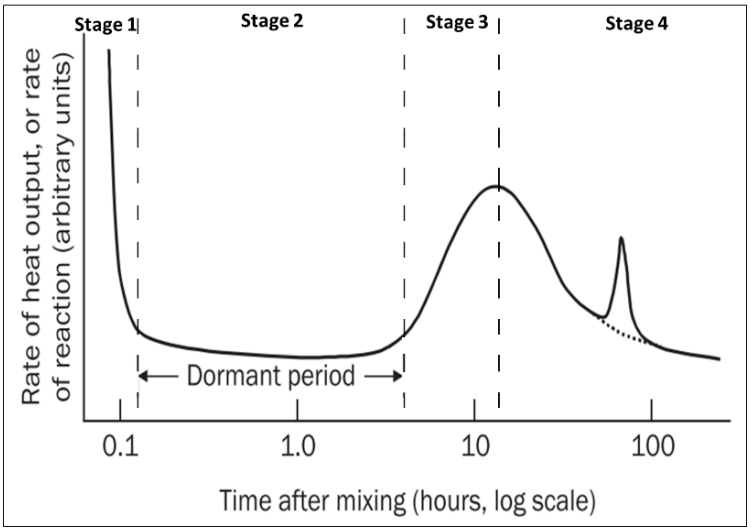


*Figure 2.1 Depiction of heat emitted during hydration due to chemical reactions over various stages of hydration (Domone and Illston, 2010)*

Stage 1 starts upon mixing when a short peak in temperature can be noticed. This peak is only for a few minutes after which the mix enters Stage 2, a dormant period for a few hours. Stage 1 is caused by the rehydration of calcium sulphate, hemihydrate, formed by the dehydration of dihydrate during the milling process as shown in the formula (All formulas are written in shorthand notation where A = $Al_2O_3$, C = CaO, F = $Fe_2O_3$, H = $H_2O$, S = $SiO_2$, Š = $SO_3$):

$$2C\check{S}(0.5H) + 3H \rightarrow 2C\check{S}.2H$$

The rehydration of the aluminates also contribute to this initial peak. The rehydration of aluminates ($C_3A$ and $C_4AF$) are particularly of interest because of its strong exothermic reaction with water. Tricalcium aluminates cause the mix to flash set when hydration thereof is unregulated (Domone and Illston, 2010). The hydration reactions of $C_3A$ depends on the availability of sulphates within the mix. In the absence of sulphates, $C_3A$ reacts directly with water, in two phases, to form calcium aluminate hydrates (Plank *et al.*, 2010):

$$\text{Phase 1: } 2C_3A + 21H \rightarrow C_4AH_{13} + C_2AH_8$$

$$\text{Phase 2: } C_4AH_{13} + C_2AH_8 \rightarrow 2C_3AH_6 + 9H$$

The first phase occurs immediately after $C_3A$ makes contact with water and if uncontrolled $C_3A$ hydration is allowed flash set occurs. The second phase takes some time compared to the first resulting in the mix containing different phases of $C_3A$ hydrates at the same time i.e. $C_4AH_{13}$, $C_2AH_8$ and $C_3AH_6$, the latter known as the cubic hydrogarnet phase (Thomas and Hamlin, 2010). However, flash setting is undesirable since time is required for placing and moulding during construction. The presence of calcium sulphate prevents the flash set of cementitious materials by initially reacting with $C_3A$ and forming ettringite, known as the AFt phase. The cause of the end of Stage 1 is due to ettringite forming a metastable layer around the cement particle preventing further dissolution (Domone and Illston, 2010). Once the sulphate:aluminate ratio falls below approximately 1.5:1, the remaining $C_3A$ reacts with ettringite to from monosulfoaluminate, this referred to as the AFm phase:

$$C_3A + 3C\check{S}.2H + 26H \rightarrow C_3A.3C\check{S}.32H$$

$$C_3A.3C\check{S}.32H + 2C_3A + 4H \rightarrow 3(C_3A.C\check{S}.12H)$$

Should the gypsum content be too low to completely react with $C_3A$, the remaining $C_3A$ hydrates directly which causes the third peak seen in Stage 4 (Bullard *et al.*, 2011). Another aluminate $C_4AF$ reacts similar to $C_3A$ but at a slower rate and does not contribute significantly to the cement behaviour. Stage 3, known as the acceleration phase is caused by the dissolution of tricalcium - and dicalcium silicates. The peak reaction rate is dominantly due to the calcium silicate reactions, specifically $C_2S$ and $C_3S$. The hydration products from these reactants provide cementitious materials with the desired characteristics of stiffness and strength, where $C_3S$ reacts much faster. $C_2S$ reacts much slower but delivers identical products (Domone and Illston, 2010):

$$2C_3S + 6H \rightarrow C_3S2\ .3H + 3CH$$

$$2C_2S + 4H \rightarrow C_3S2\ .3H + CH$$

The typical contribution of each reaction to the strength of cementitious materials over time is presented in Figure 2.2.

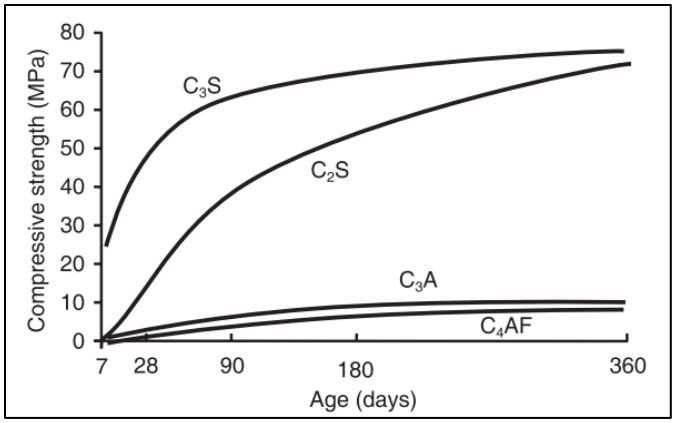


*Figure 2.2 Typical contribution of different cement constituents to the strength of cementitious materials over time (Domone and Illston, 2010).*

After a peak in reaction rate is reached hydration slowly decreases until all the available water is consumed.

## 2.1.2 Microscopic structuration process

Understanding the change in microstructure of cementitious materials is of significance as it explains the change in flow characteristics over time i.e. the rheology of cementitious materials. Figure 2.3 provides a schematization of the hydration of a single cement grain suspended in water.

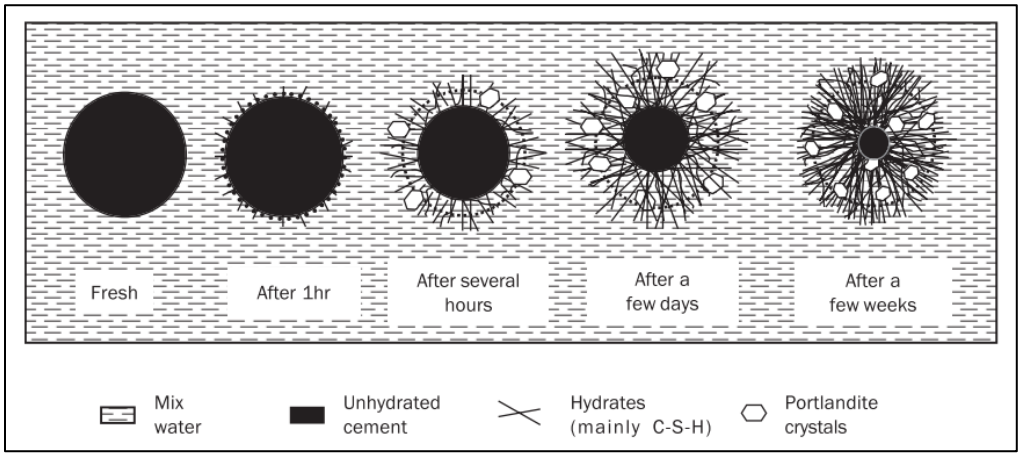


*Figure 2.3 Hydration of single cement particle suspended in water (Domone and Illston, 2010).*

The hydration process of a cement grain takes place from the outside inwards; the core diminishing as solid products build up around it. The early hydration products consists of ettringite crystals that form a barrier around the cement particle, temporarily preventing further hydration during the dormant period.

Internal pressure or the reaction with portlandite, calcium hydroxide crystals, breaks down this outer layer, ending the dormant period and allowing hydration to continue more rapidly. The products of hydration consist mainly out of portlandite crystals and fibrous particles of calcium silicate hydrate (CSH) that forms a dense fibrous matrix. However, between the fibrous matrixes many small pores are present that decrease as hydration continues and the pores are filled with new product. Theoretically a 0.43 water:cement ratio is sufficient to allow for full hydration resulting in the minimum porosity possible; in practice a water:cement ratio of 0.5 is required for full hydration of sealed specimens (Domone and Illston, 2010). As the hydration process continues the dense matrix of the individual cement particles forms flocs that entangle to form a dense matrix throughout the entire mix. It is this hydration process that results in the strength gain of cementitious materials.

### 2.1.3 Setting times

Knowing the setting time of a concrete mix used on a construction site is essential. With the setting time known, the time for mixing, transport, casting and finishing can be planned. It can also be decided whether any admixture to regulate set time is necessary. During setting cementitious materials undergo a change in chemical and physical properties that transform the mix from the plastic to solid state. Research has shown that this transition takes place at an exponential rate, where this transition can be divided into two phases. The first phase, referred to as initial setting phase, is associated with loss of workability. Once initial set has occurred the cementitious material can no longer be handled without damaging the internal structure formed during hydration. The second phase, referred to as the final setting phase, is associated with the loss of all plasticity within the cementitious material. The final setting time is therefore reached when the cementitious material becomes rigid and starts to develop strength over time (Diekmann, 2019). The setting time of concrete is influenced by various factors such as the w/c ratio, environmental temperatures, cement composition and nature of chemical admixtures used. Furthermore, the interaction between various constituents within a concrete mix can also have an influence on the setting time (Brooks, Megat Johari and Mazloom, 2000).

## 2.2 Concept of rheology

Rheology is defined as the study of the flow and deformation of matter under an applied shear stress. Rheology thus investigates material response when a shear rate is applied and considers the

shear stress-shear strain relationship. This relationship is used to describe the fluidity of a material and various models have been formulated to describe this relationship. Three commonly used models are Newton's -, the Bingham - and the Herschel-Bulkley model (Quanji, 2010).

The relationship that exists between the shear stress and shear strain is also referred to as the flow curve and forms the base for examining rheological properties. Since concrete and cement paste flows like a liquid in the fresh state, Equations 2.1, 2.2 and 2.3 can be used to describe the flow of these substances (Quanji, 2010).

$$\tau = \eta\dot{\gamma} \tag{2.1}$$

$$\tau = \tau_y + \eta\dot{\gamma} \tag{2.2}$$

$$\tau = \tau_y + K\dot{\gamma}^n \tag{2.3}$$

Where:

$\tau = Shear\ Stress\ [Pa]$

$\eta = Viscocity\ [Pa.s]$

$\dot{\gamma} = Shear\ rate\ [1/s]$

$\tau_y = Yield\ Stress\ [Pa]$

$K = consistancy\ paramater$

$n = flow\ index$

For fluids that have a linear shear stress-strain relationship in conjunction with zero yield stress, where the gradient denotes the material viscosity, Equation 2.1 is used. These fluids are called Newtonian fluids. Newtonian fluids have little to no interparticle forces thus causing the velocity gradient, induced by a shear stress, in the liquid to equal the shear rate (Quanji, 2010). Figure 2.4 illustrate the shear stress-strain relationship of a Newtonian fluid.

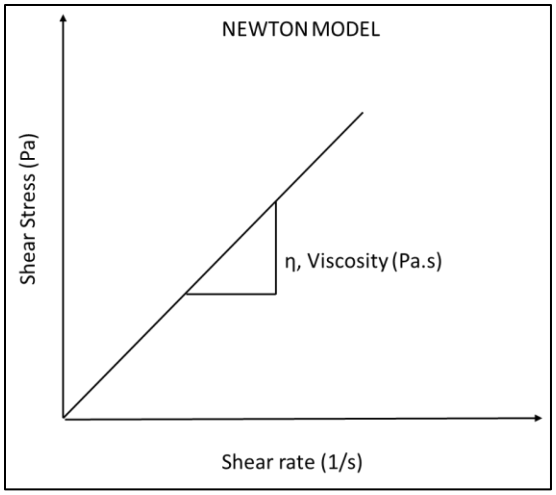


*Figure 2.4 Shear stress-strain relationship of Newtonian fluid*

Concrete and cement paste however contain strong interparticle connections and concentrated suspensions (Ferraris, 1999). Newton's law is thus not applicable to concrete and cement pastes. A second factor, the yield stress, has to be incorporated. This factor describes the stress that initiates flow once applied to the substance. The Bingham model, Equation 2.2, is thus used to described the flow of concentrated suspensions such as concrete or cement paste. The Herschel-Bulkley model, on the other hand, uses three parameters to describe the flow behaviour of concentrated suspensions as seen in Equation 2.3. Parameters K and n take into account the structuration that occurs with time in concrete and cement pastes, resulting in an exponential flow curve. Although this model is proven to best describe the behaviour of some concretes, particularly self-compacting concrete, the Bingham model is dominantly used to accurately describe the flow behaviour due to its simplicity (Ferraris, 1999). The Bingham and Herschel-Bulkley models are presented in Figure 2.5.

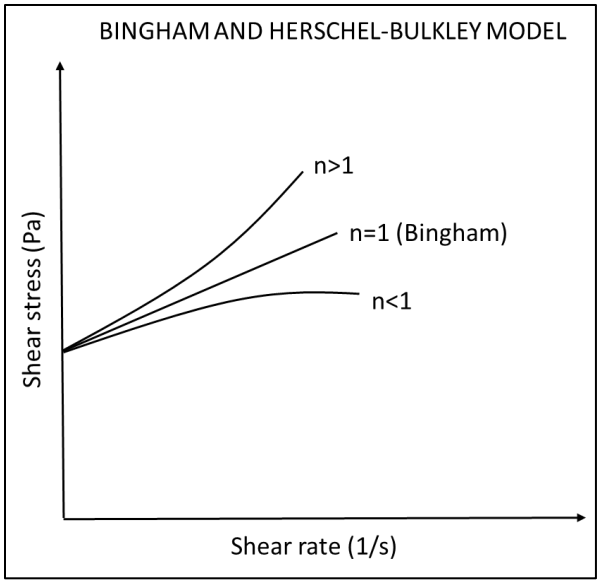


*Figure 2.5 Bingham and Herschel-Bulkley model*

## 2.3 Rheology of cementitious materials

In the construction field understanding the development of the fresh state properties of concrete is a high priority to improve productivity. Thus, understanding the influence of cement composition on the workability of concrete plays a key role. The workability of concrete can be divided into three parts (Wallevik, 2009):

- Spreadability: the ability of concrete to fill the formwork shape and cover all reinforcement while maintaining homogeneity.
- Passing ability: the ability of concrete to maintain flow through reinforcement and narrow sections without aggregate causing blockage.
- Segregation resistance: the ability of concrete to maintain homogeneity during placement and transport, thus not segregating bleeding after placement is completed.

However, workability is only one of the terms used to describe the flow behaviour of concrete. Some other terms include the mobility, flowability, consistency, finishability, stability, compactibility, pumpability etc. It should be noted that all these terms are subjective and are used to describe the flow of concrete but are mostly descriptive i.e. qualitative. These terms are thus used to describe the flow based on feeling and not from the physical behaviour of concrete.

The rheology of concrete describes the flow of concrete using quantitative parameters. The two main parameters used to describe the flow of concrete is the viscosity and yield stress. Rheological tests used to describe concrete flow behaviour measure these two parameters. Rheology therefore aims to quantify the influence of concrete constituents on the flow of concrete. Furthermore, the rheology of cementitious materials are influenced by several external factors such as temperature, humidity, shear rates etc. (Ferraris, 1999). Therefore, when the rheological properties of cementitious materials are studied it is wise to do so under the expected in-situ conditions.

The flow of concrete, being a complex suspension, can be modelled using the Bingham model, thus incorporating both the viscosity and yield stress to characterise flow. As seen in Figure 2.6 this is necessary since two concretes can have one parameter that is identical while the other differs drastically (Ferraris, 1999).

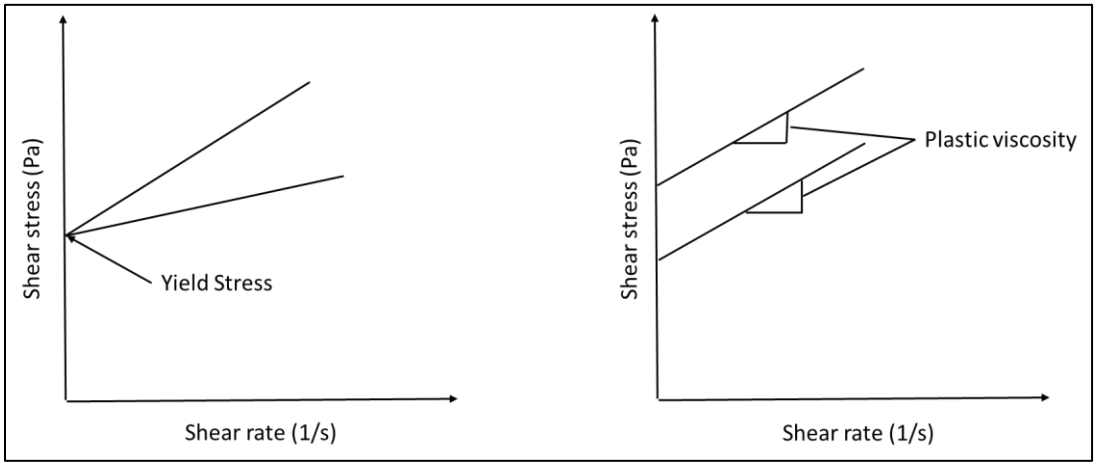


*Figure 2.6 Illustration that both yield stress and plastic viscosity is required to characterise concrete rheology* (Ferraris, 1999)

## 2.3.1 Thixotropy

The most widely accepted definition of thixotropy is the steady decrease in viscosity under shear stress after which structuration takes place once the stress in removed (Wallevik, 2009). The time dependent variation of viscosity instigated this definition of thixotropy. During the shear of cementitious materials the decrease of viscosity is caused by the change in microstructure. Particles orientate themselves in straight lines parallel to the direction of shear as the deflocculation and dispersion of cement particles occur. Various experiments exist that can be used to determine whether a substance exhibits thixotropic behaviour, the simplest of which is the thixotropic loop test. The thixotropic loop is obtained by submitting a substance to a cyclic shear stress and plotting

the stress vs shear rate as seen in Figure 2.7. If a lag in response is noticed, the substance is dependent on shear history. This method of identifying thixotropy cannot be used to obtain any quantitative data and therefore only indicates how prominent the thixotropic behaviour of a substance is (Coussot, 2012).

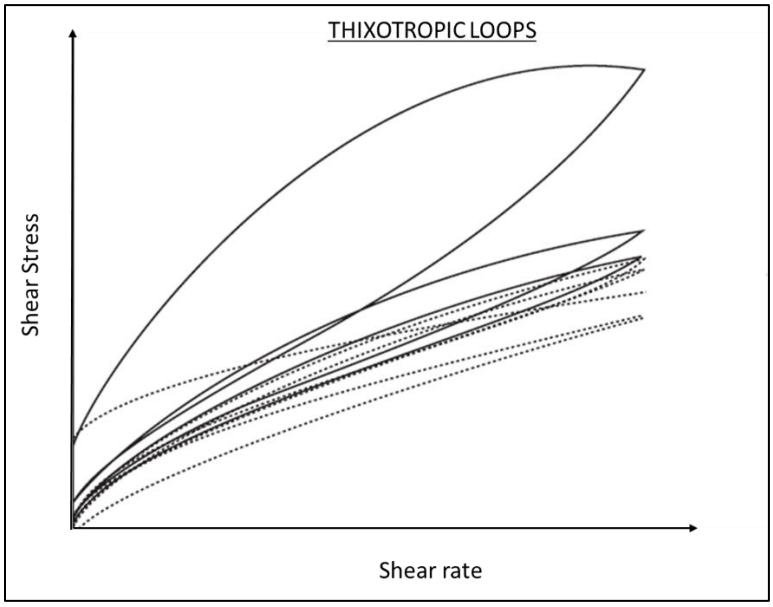


*Figure 2.7 Identifying thixotropic behaviour of cementitious materials using thixotropic loops*

Figure 2.8 provides a physical representation of thixotropy. As seen in Figure 2.8(a) cement particles are initially in a stable orientated condition due to interacting forces between them. In Figure 2.8(b) energy is added to the system via mechanical shear. If the energy added is large enough the particle will leave the energy well and initiate flow as seen in Figure 2.8(c). When additional energy is no longer applied to the system the particles will once again orientate themselves as seen in Figure 2.8(d). As the time at which cementitious materials are at rest increases the energy needed to move particles from an energy well increase.

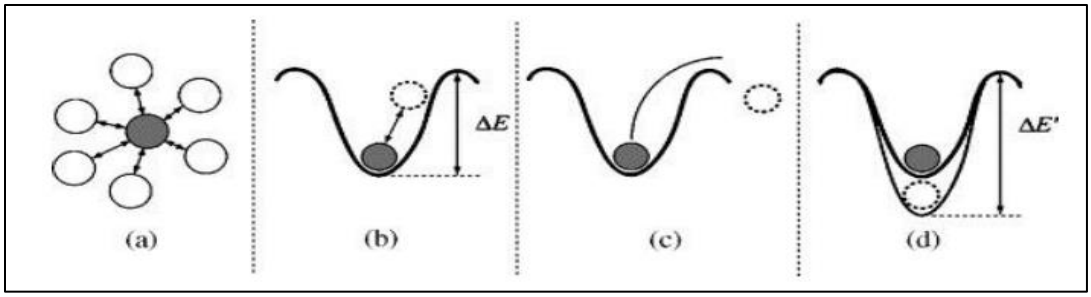


*Figure 2.8 Representation of the working of thixotropy. (a) Particles in stable state; (b)Added shear energy moves particle from stable state; (c) Shear energy is larger than attractive force between particle and flow is initiated; (d) when shear is removed particle move back to stable state (Quanji, 2010).*

The increase in energy required to move particles from an energy well can be explained by the two mechanisms from which thixotropy originates within cementitious materials over time. The first is the physical flocculation of cement particles which occurs within the first few hundred seconds once applied shear is removed. The second is the coagulation of cementitious materials due to hydration. Coagulation, in this context, therefore refers to the precipitation of solid hydration products around the hydrating cement particle through the reaction with water. Coagulation occurs over a much longer period due to hydration products causing structuration within the cement matrix. Owing to structuration taking place over much longer periods it's more prone to be influenced by environmental conditions but is dominated by the hydration kinetics of a cementitious material. Flocculation on the other hand is dominated by intermolecular forces such as attractive van der Waals forces (Kruger, Zeranka and Zijl, 2019). It can therefore be concluded that the short term thixotropic behaviour of cementitious materials is on account of flocculation whereas the long term thixotropic behaviour of cementitious materials are on account of hydration causing structuration within the cement matrix.

The measured static yield stress of cementitious materials is thus as a result of either flocculation (on short time scales) or structuration (on long time scale) depending on the time at rest. It should be noted that in practice it doesn't matter what the cause of the measured yield stress is, however for practical applications such as formwork pressures, multilayer casting and pumping pressure the yield stress is measured over several thousands of seconds. It can therefore be deducted that for practical applications thixotropy caused by hydration is more noteworthy (Roussel *et al.*, 2012).

#### 2.3.1.1 Flocculation

The evolution of cementitious materials that beget the thixotropic characteristics of cementitious materials, is illustrated using Figure 2.9. When a cementitious material is sheared cement particles are dispersed throughout the mix (Figure 2.9a). Directly after agitation is ceased, cement particles start to flocculate due to attractive forces (Figure 2.9b). At this point the material has already gained enough strength to resist stress. Even after flocculation cement particles are not in direct contact with each other due to cement particles having the same charge. There therefore exists a network of interconnected cement particles with a few nanometre gaps between them. Due to thixotropy being associated with a macroscopic change in a material's properties, the reversible deflocculation and flocculation phenomenon is often considered to be the source of thixotropy. However for cementitious materials this is not the only source of thixotropy (Roussel *et al.*, 2012).

#### 2.3.1.2 Structuration

Flocculation of cement particles occur within a few hundred seconds, however the cementitious materials keep gaining strength in the semi-liquid phase for several thousands of seconds, resulting in an increase in elastic modulus (or yield stress), during the dormant period. This is due to calcium silicate hydrate (CSH) bridges forming at the quasi contact points between particles after flocculation (Figure 2.9c). The further increase in elastic modulus over time is as a results of these CSH bridges increasing in number and size (Figure 2.9d). As this increase in CSH bridges occurs during the dormant phase, a linear increase in elastic modulus occurs over time. The rate of increase in elastic modulus does however decrease over time. This increase in elastic modulus causes a corresponding increase in yield strength (Coussot, 2012). The thixotropic behaviour in cementitious materials are thus responsible for the change in yield stress over time. Even though the chemical reaction that results in the formation of the CSH bridges is not reversible on a microscopic level, the macroscopic effect thereof on the yield stress over time is reversible, as long as the particle bonds throughout the entire matrix is weak enough to be broken by the applied shear stress. These particle bonds form again once shear is ceased providing the chemical reactants required for the formation thereof are still available within the concrete solution (Roussel *et al.*, 2012).

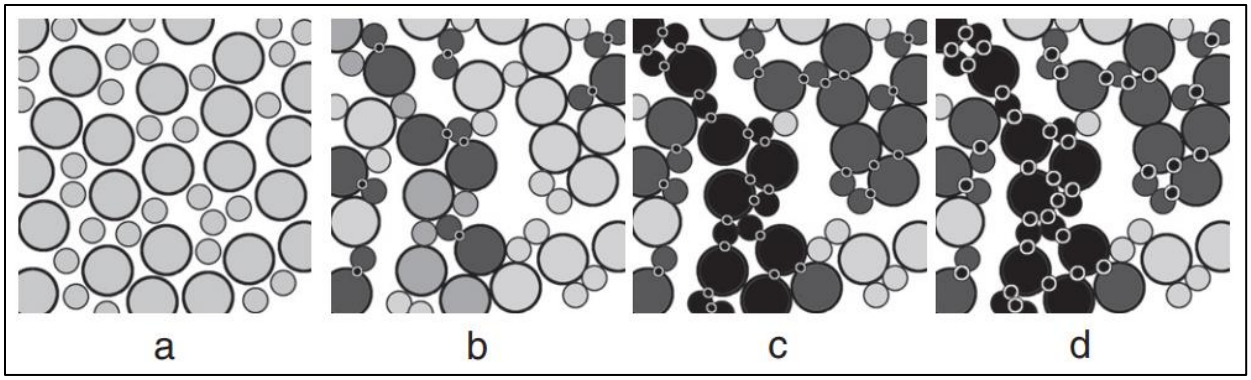


*Figure 2.9 Evolution of cementitious materials from which thixotropy originates. (a) Cement particles flocculate; (b) After flocculation CSH bridges start to form at quasi contact points; (c) CSH bridges increase over all contact points (d) CSH increase in number and size causing the cementitious material to stiffen in the fresh state (Roussel et al., 2012).*

### 2.3.2 Viscosity

Viscosity is defined as a materials' characteristic to resist flow, after yielding, when an external stress is applied. This resistance against flow is caused by internal friction and interparticle bonds. The viscosity of cementitious materials are not constant but vary with time. This time dependent behaviour of apparent viscosity of cementitious materials can be explained by considering the mechanisms responsible for structuration during rest. The dispersion of flocs and/or breakdown of agglomerates produce the measured apparent viscosity within cementitious materials (Roussel *et al.*, 2012). Seeing that only flocculation contributes to the internal structure at the early age of cementitious materials the minimum viscosity is measured with initial shear. This explains the reduction in apparent viscosity of cementitious materials with the addition of Water Reducing Agents (WRA), seeing that plasticisers and superplasticiser facilitate the dispersion of flocs. However, the apparent viscosity is also dependent on the applied shear stress. An increase in applied shear stress increases the degree of breakdown resulting in a smaller apparent viscosity being measured. Once flocculation has taken place and hydration starts the internal structure of cementitious materials start to build resulting in strength gain. This causes an increase in apparent viscosity over time as more energy is needed to initiate flow (Umeya, 1980). The apparent viscosity is used as an indication of a materials resistance to flow in the so called solid liquid phase i.e. before flow is initiated and the material deforms within the elastic region. Once a material reaches its yield point and flow is initiated the materials resistance to flow is expressed as the plastic viscosity (Abduo *et al.*, 2016). The plastic viscosity of concrete is critical to understand as

it gives an indication of concrete workability, durability, susceptibility to segregation and mechanical properties.

Various plastic viscosity prediction models, either phenomenological or fundamental, have been suggested over the years. Phenomenological models are derived from observations such as deLarrard and Ferraris's model that predicts that plastic viscosity is solely dependent on particle packing density. However, these models were found to be inefficient in predicting the plastic viscosity of cementitious materials. This is due to these models not taking suspension with high concentrations of particles into account as is the case with concrete. These models therefore ignore particle interaction, thixotropy and the structuration of concrete over time. On the other hand, fluid mechanics and rheology science form the basis of fundamental models. Although these models are time consuming, they have been proven to deliver dependable results and can be used to determine concrete plastic viscosity (Chidiac and Mahmoodzadeh, 2009).

### 2.3.3 Yield stress

Two forms of fluids can be identified in terms of yield strength characteristics as mentioned in Section 2.3.1. Simple yield stress fluids (SYSF) exhibit one yield stress $\tau_y$. When a stress smaller than $\tau_y$ is applied, assuming the material is in liquid state, flow will not continue. The opposite is also true for SYSF i.e. should the material be in a solid state and a stress larger than $\tau_y$ is applied to the material, flow will be initiated. The yield stress of a material can be identified by examining the flow curve of SYSF. The yield stress is reached when the shear rate decreases to zero. The yield stress can be measured by applying a constant shear rate $\dot{\gamma}$. The stress-strain curve of a SYSF exhibits two regimes, a linear regime at low strains after which the curve flattens out to a stress plateau. The curve flattens out once the yield stress, corresponding with the yield strain $\gamma_y$, is reached and flow is initiated (Ovarlez, 2011).

On the other hand materials that exhibit flow behaviour described by the Bingham or Herschel-Bulkley model, as is the case with cementitious materials, are classified as yield stress fluids (YSF). These materials exhibit viscous-elastic behaviour. During low stress conditions the material exhibits dominantly elastic behaviour with the elastic modulus $G'$ being far greater than the viscous modulus $G''$. When stress is increased to $\tau_y$, $G'$ decreases and $G''$ increases to a maximum. The yield stress associated with the change from solid to liquid state in YSF is called the static yield

stress (SYS or $\tau_{y_S}$). After the SYS is reached, shear stress and the material viscosity, decreases with increasing strain until a stress plateau is reached. This stress plateau corresponds with the dynamic yield stress (DYS or $\tau_{y_D}$) of an YSF (Ovarlez, 2011). This behaviour of YSF is due to its thixotropic properties. Figure 2.10 illustrates the difference in stress-strain relationship between SYSF and YSF.

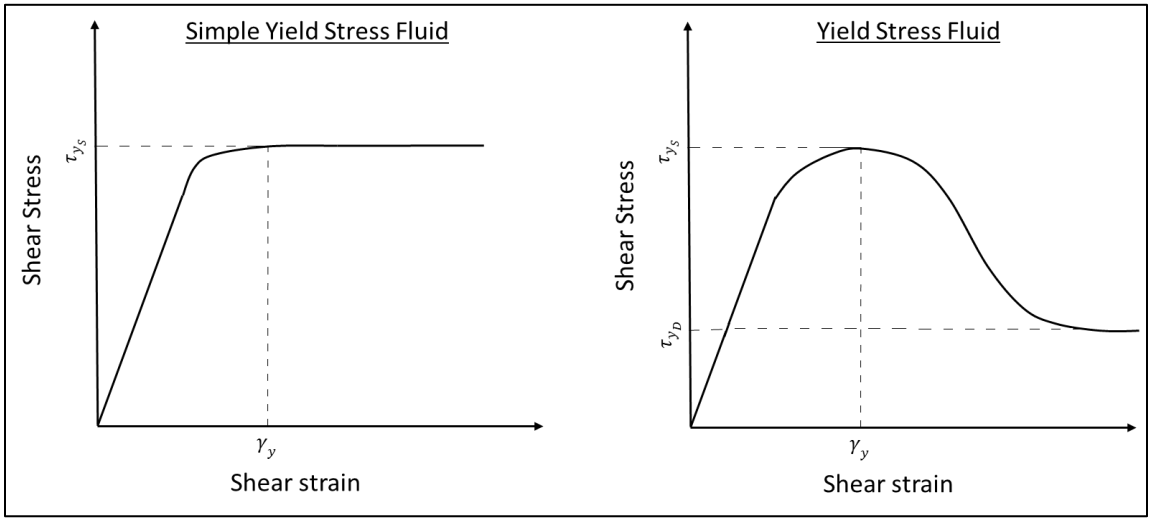


*Figure 2.10 Illustration of difference in stress-strain relationship between SYSF and YSF*

## 2.3.4 Practical application of rheological parameters

The rheological properties of concrete can be manipulated to manage various aspects in concrete construction such as pumping pressure, surface finish, formwork pressure, segregation etc. Yet, empirically derived tests such as slump flow, L-box, V-funnel and J-ring tests are more commonly used to give an indication of the rheological properties of concrete instead of using tests based on fundamental principles that directly measure the rheological parameters of concrete. Rheological tests based on fundamental principles are specifically applicable to mixes with high fluidity, were the flow is governed by own weight (Ferraris *et al.*, 2017).

High fluidity in concrete mixes, made possible through the use of plasticiser/superplasticiser, are often desired to ease placing and improve finish quality. However, if the fluidity of a mix is increased beyond its capability segregation occurs. This is undesirable as it causes non-homogeneity due to aggregate settling to the bottom of the mix or excessive water migrating to the surface of the concrete. These non-homogeneities lead to undesirable fresh state and mechanical properties of the concrete. To ensure that a concrete has adequate segregation resistance the yield

stress and plastic viscosity should be elevated. Furthermore, the thixotropy of concrete can also be utilised to reduce segregation. If a concrete with low yield stress is desired, a high thixotropy will help minimise segregation as the mix re-flocculates quickly with time, preventing further settlement of aggregate (Ferraris *et al.*, 2017).

Furthermore, inappropriate concrete rheological properties can present problems during pumping, causing blockage of pipelines or build-up of pressure. Although there are several aspects that influence the pumpability of concrete such as the pipeline thickness and pump flow rate, lowering the viscosity of concrete has been proven to effectively lower pressure during pumping. A high yield stress can also increase pumping pressure, however viscosity has been shown to be dominant in determining the pumpability of concrete (Ferraris *et al.*, 2017). The control of concrete pumpability can save both project cost and time.

Controlling the rheological parameters of concrete can also be valuable in limiting formwork pressure. Conventional concrete has a high yield stress and thixotropy that results in relatively low formwork pressures (Ferraris *et al.*, 2017). However, it is due to these properties that vibration is needed for proper consolidation of conventional concrete. On the other hand, concrete with high fluidity such as SCC has to consolidate under own weight. This is desired as it results in faster casting rates. However, a highly flowable concrete has a low yield stress which results in high formwork pressures. This can cause formwork to deform or collapse and designing formwork that can withstand these high pressures can cause a considerable increase in project cost. Thixotropy plays a key role in minimising this disadvantage. By increasing the thixotropic behaviour of SCC the induced hydrostatic pressures are reduced as the concrete forms an internal structure once at rest and starts to support its own weight. Multi-layer casting is also used to overcome the challenge of high formwork pressures. When this construction method is used the thixotropy of concrete again plays a key role. Each layer of concrete has a short period to gain strength before the next layer is cast. If the thixotropy of the concrete is too high the yield stress will increase rapidly above a specific point and prevent the two layers from mixing and bonding, resulting in a weak interface between the two layers (Roussel, 2006).

The rheology of concrete can also be utilised to enhance the aesthetics of concrete with regard to surface finish. Colour homogeneity, surface roughness and reproduction of formwork details are only some of the aesthetical issues that can be addressed by controlling the rheology of concrete.

To ensure that the desired surface finish is obtained it is necessary to obtain a balance between the yield stress and viscosity. If the viscosity of concrete is too low it could result in segregation and lead to uneven distribution of aggregate, whereas a too high viscosity and yield stress will slow down unwanted air bubbles from rising to the surface and could cause 'bug holes'(Ferraris *et al.*, 2017).

It should be noted that adjusting the rheological properties of concrete to achieve one goal could be disadvantageous to other aspects of concrete performance. The use should thus be taken into account during concrete design. A summary on how the rheology of concrete governs performance is presented in Figure 2.11.

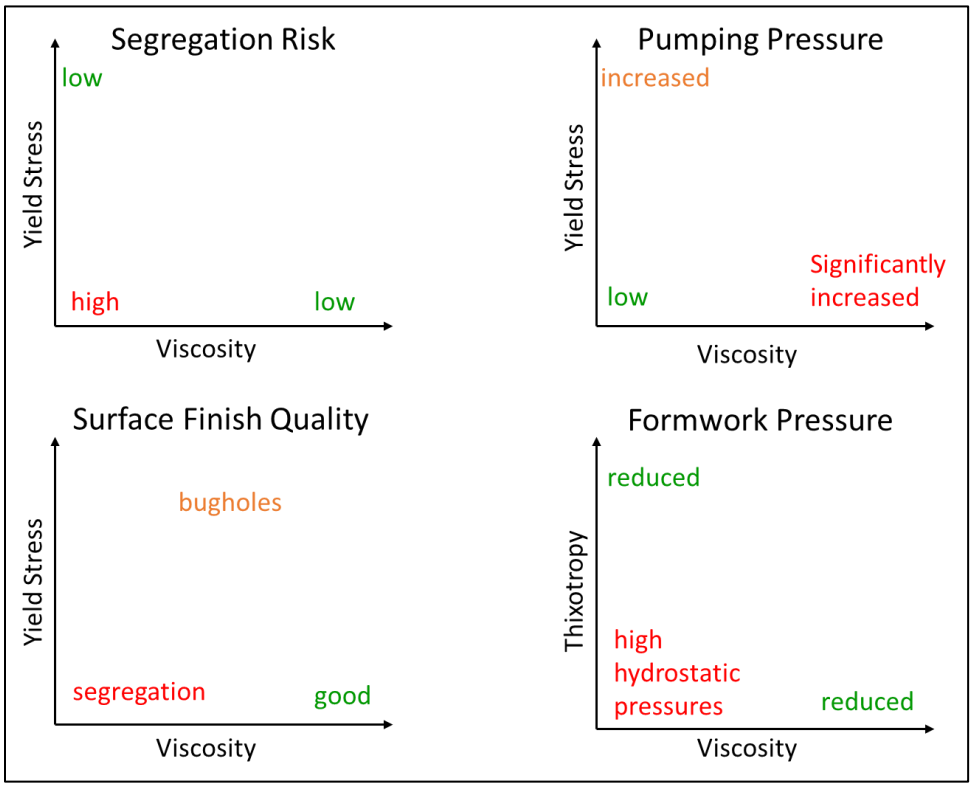


*Figure 2.11 Summary of how the rheology of concrete governs performance* (Ferraris *et al.*, 2017)

## 2.4 Characterisation of yield stress for thixotropic fluids

Thixotropic substances are distinguished by their behaviour depending on the flow history of the material. To characterise thixotropic substances a series test are performed, the period over which test are performed, depending on whether properties in the liquid of solid state are of importance.

Some tests used to characterise the properties associated with thixotropic fluids are described in the following sections.

## 2.4.1 Liquid state properties

Thixotropic substances maintain a liquid state when experiencing a shear stress larger than the materials dynamic yield stress. The dynamic yield stress is used to understand how a fluid reacts after shear.

### 2.4.1.1 Flow curve test

One test used to describe the dynamic yield stress, $\tau_{Y_D}$, and occurrence of viscosity bifurcation of thixotropic substances is the flow curve test. The flow curve test is performed by applying a range of constant shear strain rates to a substance over a time period until a constant shear stress is reached. If a shear strain rate induces a shear stress lower than the yield stress an elastic response is observed. The dynamic yield stress is the minimum stress required to reach steady flow. Since thixotropic substances are dependent on flow history they should be presheared at a high shear rate to induce a steady state which ensures that all tests are performed from the same destructured state. In contrast with SYSF, thixotropic YSF could take long to reach a steady state and steady shear rates that are achieved at shear stresses close to $\tau_{Y_D}$ are typically higher than the critical shear rate of the substance. However, for SYSF's the shear rate tends to zero as the shear stress strives to $\tau_{Y,d}$. During shear rate controlled experiments it is important to note that the stable flow cannot be induced unless the shear rate is larger than the critical shear rate $\dot{\gamma}_c$ for thixotropic materials. A selected shear rate is larger than $\dot{\gamma}_c$ when stable homogeneous flow is observed throughout the sample. Rheometric equations should be used to calculate the macroscopic shear rate of a substance. For a macroscopic shear rate lower than $\dot{\gamma}_c$ the substance undergoes shear banding, a phenomenon were the substance divides into two regions, one static and the other flowing at $\dot{\gamma}_c$. Therefore data obtained using a macroscopic shear rate lower than $\dot{\gamma}_c$ cannot be used since the substance responds heterogeneously (Ovarlez, 2011).

### 2.4.1.2 Shear rate step test

Although the flow curve test can be used to give an indication of material structuration during shear by measuring the time required to reach steady state, the shear rate step test gives a clearer indication thereof. The test is performed by inducing shear in a substance until a steady state is

reached. A new shear rate is then abruptly enforced upon the substance until it returns to a different steady state. By plotting the shear stress versus time the substance response to a change in shear can be studied. From this graph the destructuration/structuration characteristic of the substance due to dispersion and agglomeration of flocs can be determined. If an increase in shear rate is enforced the shear stress response characterises destructuration, while a decrease in shear rate characterises structuration within the substance. Figure 2.12 illustrates the typical response in shear stress of a thixotropic substance when introduced to a change in shear rate (Ovarlez, 2011).

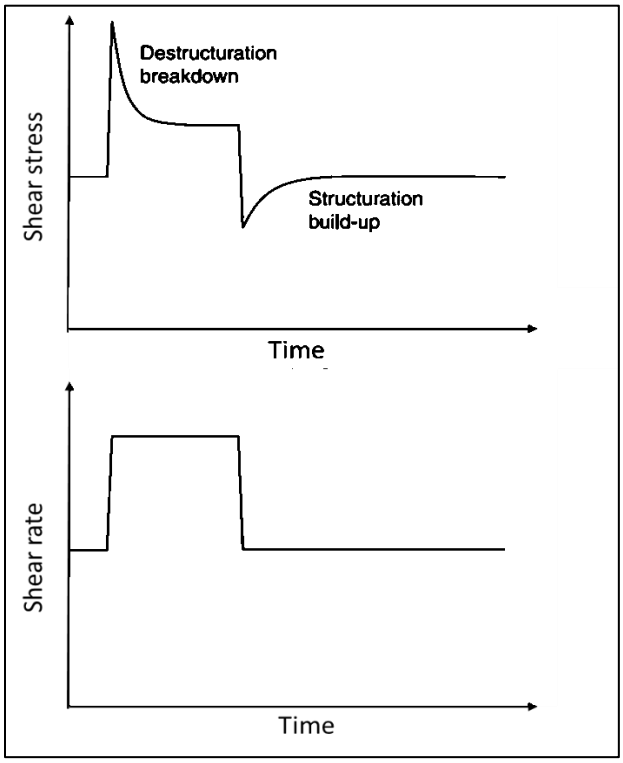


*Figure 2.12 Shear stress response to change in shear rate (Ovarlez, 2011).*

The shear stress response is commonly modelled by an exponential equation which is used to determine the time required for deflocculation/re-flocculation.

### 2.4.2 Solid state properties

Cement paste and concrete becomes structured as they age i.e. with time. This aforementioned characteristic causes the static yield stress and elastic modulus of the substance to increase if permitted time to rest (Ovarlez, 2011). Various methods exists for studying the structuration of these substances over time.

To study the structuration of thixotropic substances at rest it is important to establish an initial state. This is necessary since the macroscopic behaviour of thixotropic substances, in the solid state, is strongly dependent on the shear history. To overcome this characteristic the substance should be presheared at a high shear rate to ensure that each test starts from the same destructured state and allowed a pre-set period to rest and subsequently age. Rest is defined as the period while zero stress is applied to the substance (Ovarlez, 2011).

### 2.4.2.1 Static yield stress

The static yield stress of a thixotropic substance increases when at rest thus increasing in resistance to flow and becoming more viscous. The shear stress of a thixotropic substance initially increases approximately linear with an increase in strain, the slope increasing with increasing time of rest. As strain increases past a certain point, referred to as the yield strain the shear stress will slowly decrease as the substance undergoes de-flocculation. Shear stress will decrease to the dynamic yield stress independent of the time of rest before testing. The static yield stress is the point of maximum shear stress. To study the influence of time on static yield stress tests should be repeated for various resting times i.e. reflocculation times. The typical shear stress-strain relationship and growth in yield stress, with increasing rest time, is illustrated in Figure 2.13. The quantitative increase in static yield stress is often in relation to the increase in elastic modulus although studies have indicated that this is not always the case for cement pastes and concrete (Ovarlez, 2011).

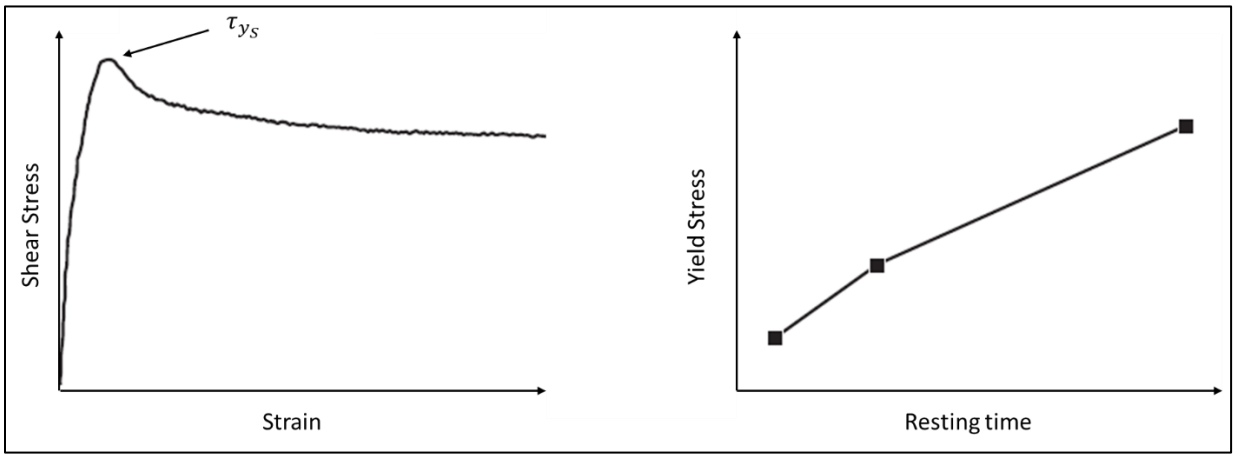


*Figure 2.13 Typical shear stress-strain relationship and growth in yield stress with increasing time of rest (after Ovarlez, 2011)*

### 2.4.2.2 Elastic modulus

Once a steady destructured state is defined the re-flocculation and structuration of the substance is studied through the use of oscillatory experiments. Viscoelastic behaviour is often observed for

YSF's in the solid state. A linear stress-strain relationship is obtained when low strains are applied, defining the elastic modulus as $G = \frac{\tau}{\gamma}$. However, thixotropic substances also exhibit a viscous component thus delaying elastic behaviour. To separate and evaluate elastic and viscous behaviour strain oscillations are applied according to Equation 2.4 and the stress response is measured as seen in Equation 2.5 as long as the substance is strain within its linear regime (Ovarlez, 2011).

$$\gamma(t) = \gamma_o \sin \omega t \qquad 2.4$$

$$\tau(t) = G'(\gamma_o \sin \omega t) + G''(\gamma_o \cos \omega t) \qquad 2.5$$

As seen from Equation 2.5 the elastic modulus, $G'$, is in phase with shear strain, Equation 2.4, whereas the viscous modulus, $G''$, is in phase with strain rate. Structuration is verified by the increase in the elastic modulus with time as depicted in Figure 2.14 (Ovarlez, 2011).

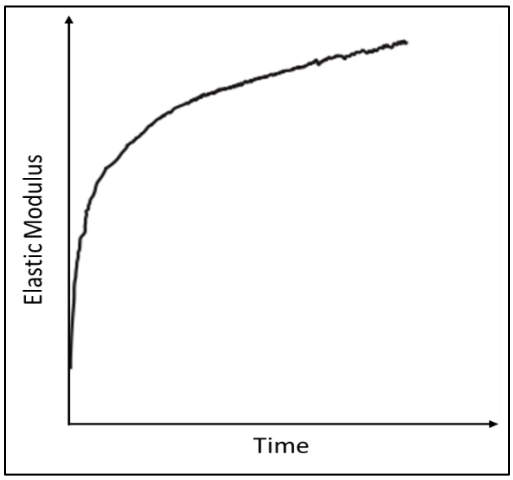


*Figure 2.14 Gain in elastic modulus over time due to structuration for cement paste (Ovarlez, 2011).*

Care should be taken to ensure that the applied oscillations doesn't change the material state. This is done by ensuring that the applied oscillations stress the material within the linear regime as the application of oscillations in the non-linear regime effect the rate of re-flocculation (Ovarlez, 2011).

## 2.5 Plasticiser / superplasticiser

Modern day concrete is engineered to obtain desired characteristics. Superplasticisers are one example of chemical admixtures used to modify the fresh state properties of concrete. Superplasticisers, also referred to as high range water reducers, can reduce concrete water demand by 15-30%. They are therefore used to provide workability at low w/c ratios or maintain a desired

w/c ratio while increasing fluidity i.e. workability. This is achieved by the superplasticisers consisting of a long organic polymer chain with attached sulphonate, hydroxyl or carboxylate groups containing negatively charged ions that result in the superplasticisers having an affinity for water. It is the degree of polymerisation and structure of the superplasticiser that determines its efficiency in cement particle dispersion. The influence of superplasticisers on the w/c ratio and fluidity of a mix have made them a key component in the design of high performance and self-compacting concrete. A reduction in w/c ratio results in more durable, stronger concrete whereas an increase in fluidity allows for concrete placement in between dense rebar and increased pumpability due to a low plastic viscosity (Chakkamalayath *et al.*, 2011).

Plasticisers/superplasticisers can be divided into four groups based on their composition that is; lignosulphonates (LS), Sulphonate melamine formaldehydes (SMF), sulphonate naphthalene formaldehydes (SNF) and polycarboxylic ethers (PCE). LS are also referred to as first generation superplasticiser, SNF and SMF as second and PCE as third generation superplasticisers, SNF and PCE being the most commonly used superplasticisers today. Although the cost of these two superplasticisers are more than that of SMF and LS they are often used in smaller dosages to achieve a desired fluidity (Chakkamalayath *et al.*, 2011).

### 2.5.1 Working mechanisms

The forces influencing concrete rheology are van der Waal's and electrostatic repulsion forces. Electrostatic repulsion is caused by the cement particles having positive surface charges. However, van der Waal's forces between cement particles are stronger than electrostatic repulsion forces resulting in attractive forces between cement particles that cause flocculation. Superplasticiser is utilised to delay flocculation, therefore increasing fluidity (Chakkamalayath *et al.*, 2011).

Plasticiser/superplasticisers interact with cement pastes in three ways. The first is the absorption of plasticiser/superplasticiser within the hydrating cement particle, during the formation of ettringite, resulting in the decrease in active dosage available for particle dispersion. This phenomena is usually negligible depending on the absorption of the mix and can be minimized by delaying the addition of plasticiser/superplasticisers. The second interaction is due to the respective charges of cement particles and plasticiser/superplasticisers. The surface of cement particles are positively charged. Negatively charged plasticiser/superplasticiser particles therefore bind with the positively charged cement particle, forming an electrical double layer. The electrical double layer

results in repulsive forces between particles causing dispersion of flocs. The dispersion of flocs releases entrapped water therefore increasing mix fluidity and reducing water consumption of the mix. This interaction between plasticiser/superplasticiser and cement pastes are observed by the addition of LS, SMF and SNF where the electrostatic repulsion forces are proportionate to the dissolution of plasticiser/superplasticiser and cement paste composition. The electrostatic repulsion forces diminish over time allowing cement particle to flocculate which results in mix stiffening. In addition to electrostatic repulsion forces, PCE molecules cause steric hindrance between cement particles. Steric hindrance contributes to dispersion of flocs, the steric forces depending on the main chain and side chain length as well as the amount side chains. The PCE molecule binds with the cement particle via its backbone resulting in the sidechains of the molecule to be directed outwards into the mix solution, causing flocculated particles to disperse. High slumps and slump retention are therefore possible at low dosages of PCE. The third way in which superplasticisers increase concrete workability is through non-absorbed particles. These particles lubricate cement particles, reducing friction via the arrangement of polymer chains parallel to the direction of flow. Furthermore, these particles reduce the water surface tension within the mix allowing for greater dispersion of cement particles (Chakkamalayath *et al.*, 2011).

### 2.5.2 Influence on fresh state properties

Lignosulphonates are often used due to their low cost, however relatively high dosages are required to obtain a desired slump. LS are also known to cause air entrainment and retardation in concrete. SMF are efficient in obtaining high initial slump but are not appropriate if slump retention is required. These superplasticisers are therefore generally used to create precast concrete that is cast in short time spans. On the other hand SNF are commonly used in ready mix concrete due to their slump retention properties, making concrete suitable for transfer over long distances. However, these superplasticiser are known to have unpredictable behaviour. PCE are the most effective in water reduction, being used to reduce the water content by as much as 40% in some cases. This makes PCE suitable for the design of high strength and self-compacting concrete. PCE is known for causing good slump retention without effecting the rate of strength gain (Chakkamalayath *et al.*, 2011). The behaviour of LS and PCE plasticiser/superplasticisers were confirmed in a study conducted by Katimi, 2017. The study concluded that LS can be used in the design of ready mix concrete due to the plasticiser/superplasticiser causing an increase in initial set time while PCE

causes high reduction in water consumption within a mix without reducing set time, therefore making it suitable for high strength concrete.

### 2.5.3 Influence on solid state properties

The early strength gain of cementitious materials are dominated by the hydration of $C_3A$ and $C_4AF$ while the hydration of $C_3S$ and $C_2S$ dominate the strength gain thereafter. The use of WRA influences these hydration processes causing a change in strength gain characteristics. LS type plasticisers have a greater affinity to the aluminate hydration phase. This results in LS affecting the fresh state properties of cementitious materials without influencing strength gain. However, if insufficient proportions of $C_3A$ and $C_3AF$ are within the mix, the admixture bonds with $C_3S$ and $C_2S$, causing delayed hydration thereof resulting in delayed strength gain (Aydin, 2017). The presence of SMF and SNF based superplasticiser causes a respective increase and decrease in concrete compression strength. According to Singh, Sarvahi and Singh (1992) this can be explained by considering the influence of these superplasticisers on the microstructure of cementitious materials. It is found that SMF based superplasticisers cause a decrease in pores present within the cementitious material whereas the opposite is true for SNF based superplasticisers. The study continues to predict that this is due to SNF superplasticiser being more readily absorbed onto the surface of hydrating cement particles, changing the morphology of CSH. PCE based superplasticiser are also found to effect the strength gain of cementitious materials. Pirazzoli *et al.* (2005) found that the addition of PCE based superplasticisers increase the degree of early tricalcium silicate hydration, the degree being dependent on the main chain and side chain length of the superplasticiser.

Although a great deal of studies have been conducted to predict the performance of superplasticisers, compatibility issues still arise frequently. This is because of the many factors influencing cement-superplasticiser compatibility. Plasticiser/superplasticiser as well as cement composition have to be taken into account, form of set retarder used e.g. anhydrite, dihydrate or hemihydrate and the fineness of the cement.

## 2.6 Cement composition – plasticiser/superplasticiser incompatibility

In the modern construction industry a multitude of different cement forms, mineral and chemical admixtures exists with no clear guideline on how they should be used in conjunction with each

other. A trial and error approach is therefore adopted to determine the amount of chemical or mineral admixture required to obtain desired mix properties. The expected behaviour of various chemical or mineral admixture on concrete rheology is depicted in Figure 2.15.

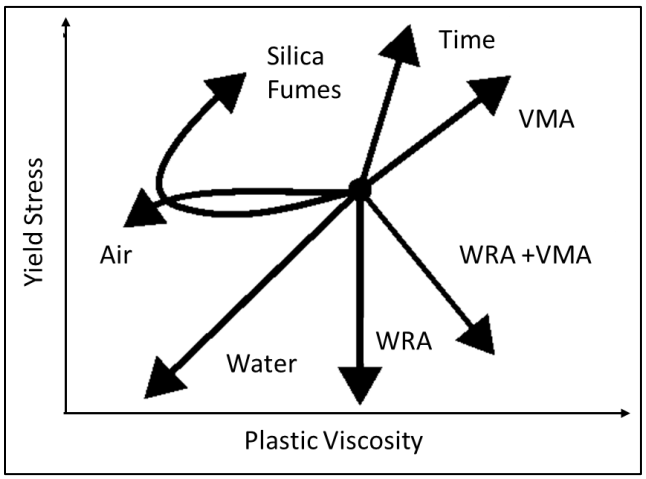


*Figure 2.15 Expected influence of various constituents on concrete rheology* (Ferraris *et al.*, 2017)

Project specific mixes are thus designed without taking variability in project conditions or cement constituents, throughout the length of the project, into account. This results in compatibility issues arising that can cause project delays and loss of profit. Compatibility issues that arise from improper cement-superplasticiser combinations include rapid slump loss, retardation, slow strength gain etc. Many of these compatibility issues can be interrelated to the way superplasticisers interact with cement and how this interaction influences the fresh state properties and hydration of concrete. The influence of superplasticiser on the rheology of concrete is dependent on the absorption characteristics of the cement mixture in combination with superplasticiser composition (Ferraris *et al.*, 2017).

## 2.6.1 Type of calcium sulphate

Calcium sulphate in the form of gypsum is added to clinker during the milling phase, the temperature at milling determining the type of calcium sulphate present in cement i.e. dihydrate (gypsum), hemihydrate (basanite) or anhydrite (Chakkamalayath *et al.*, 2011). Gypsum, or dihydrate, is a naturally occurring calcium sulphate having a chemical composition: $CaSO_4.2H_2O$. Hemihydrate and anhydrite are a result of gypsum dehydration at different temperatures (Camarini and De Milito, 2011):

$$CaSO_4.2H_2O \xrightarrow{>100^{\circ}C;<180^{\circ}C} CaSO_4.0.5H_2O + 1.5H_2O$$

$$CaSO_4.2H_2O \xrightarrow{>300^{\circ}C} CaSO_4 + 2H_2O$$

Clinker is usually milled using ball mills, during which dihydrate is added as a set regulator. During grinding a lot of energy in the form temperature is generated. Although water or air cooling is often used to limit temperatures during this milling process the dehydration of dihydrate to hemihydrate, and to a lesser extent anhydrite, occurs naturally during the milling process of clinker due to spikes in temperature at localised areas in the mil (*Cement Milling*, 2019).

It has been found that the main influence of the temperature during milling on cement quality can be related to the dehydration of dihydrate to hemihydrate. This dehydration of dihydrate to hemihydrate particularly influences the setting time and susceptibility to false set of cementitious materials (Suzakawa and Kobayashi, 1966). The source of sulphate in a cement is important because of the difference in rate of dissolution. Hemihydrate has the highest dissolution rate followed by dihydrate and then anhydrite, the dissolution rate of anhydrite being considerably lower than that of dihydrate (Lee *et al.*, 2019).

García-Maté *et al.*, (2015) investigated the influence of the sulphate source on the hydration of eco-cement. It was found that the use of hemihydrate caused the shortest initial setting time whereas anhydrite caused the longest initial setting time. It was concluded from the study that this is as a result of the faster dissolution of hemihydrate resulting in earlier formation of ettringite. The type of calcium sulphate present in cement also influences the morphology of ettringite crystals. From Figure 2.16 it can it observed that dihydrate produces a matrix of long prismatic ettringite crystal with a high degree of voids, whereas hemihydrate produces densely packed matrix of short ettringite needles at the same concrete age.

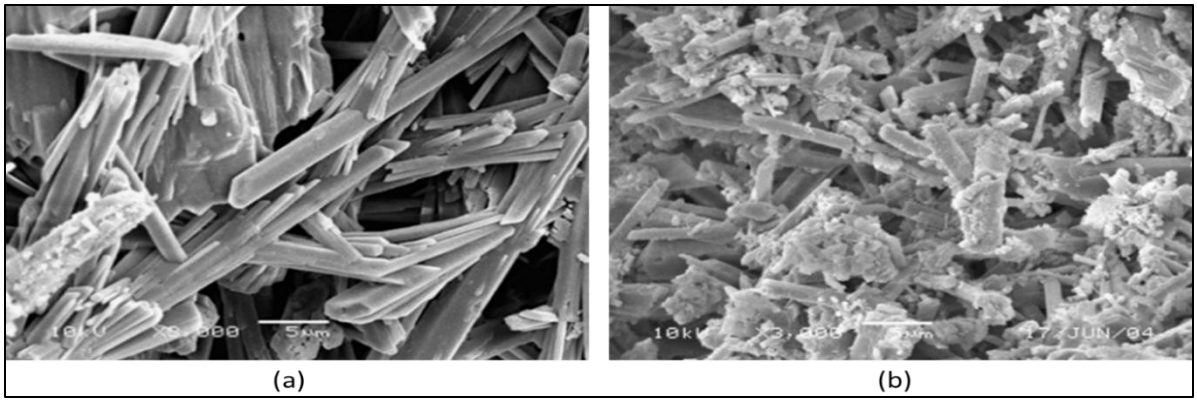


*Figure 2.16 SEM images of ettringite growth in a) dihydrate-cement and b) hemihydrate-cement pastes* (Camarini and De Milito, 2011).

### 2.6.1.1 Tricalcium aluminates

Although present in small quantities, tricalcium aluminates form an important component of Portland cement and the unregulated hydration thereof can cause flash set of a mix. The normal, false, quick or flash set of a cementitious materials due to the hydration of $C_3A$ is dependent on both the reactivity of the $C_3A$ and availability of soluble sulphates (Chakkamalayath *et al.*, 2011). Normal setting occurs when the hydration of $C_3A$ occurs in combination with calcium sulphate to from ettringite / monosulfoaluminate, the quantity influencing the rheology of a mix. A sulphate / tricalcium aluminate molar ratio of 0.75 is theoretically required to convert all $C_3A$ to monosulfoaluminates (Plank *et al.*, 2010). Flash set occurs when an inefficient quantity of calcium sulphate, with inefficient dissolution rate or solubility is used and $C_3A$ converts to its cubic hydrogarnet phase, as discussed in Section 2.1.1, instead of ettringite. False set occur when excess sulphate is present and gypsum crystallization follows (Rößler *et al.*, 2007). Table 2.1 summarises the chemical reactions that occur, for various sulphate / tricalcium aluminate molar ratios, between the aforementioned reactants (using the shorthand notation described in Section 2.1.1).

*Table 2.1 Calcium sulphate – tricalcium aluminate reaction*

| **Flash Set** | **Normal hydration** | | | **False set** |
|---|---|---|---|---|
| CaŠ/C3A molar ratio << 0,75 | CaŠ/C3A molar ratio < 0,75 | CaŠ/C3A molar ratio = 0,75 | CaŠ/C3A molar ratio > 0,75 | CaŠ/C3A molar ratio >> 0,75 |
| -$C_3A$ + 3CŠ.2H + 26H → $C_3A$.3CŠ.32H<br>-$C_3A$.3CŠ.32H + 2$C_3A$ + 4H → 3($C_3A$.CŠ.12H)<br>-2$C_3A$ + 12H → 2$C_3AH_6$ | | -$C_3A$ + 3CŠ.2H + 26H → $C_3A$.3CŠ.32H<br>-$C_3A$.3CŠ.32H + 2$C_3A$ + 4H → 3($C_3A$.CŠ.12H) | -$C_3A$ + 3CŠ.2H + 26H → $C_3A$.3CŠ.32H<br>-Ca+2 + $SO_4^{-2}$↔ CaŠ | |

Pourchet *et al.* (2009) found that the type of the calcium sulphate modifies the products of tricalcium aluminate and calcium sulphate hydration as well as the rate of hydration. The study found that the formation of $C_4AH_{13}$ and $C_2AH_8$, which are the metastable hydration products of tricalcium aluminates in the absence of calcium sulphates, don't form in the presence of hemihydrate due to its faster rate of dissolution. However, these intermediate products of tricalcium aluminate hydration are present when dihydrate i.e. gypsum, is used as a source of calcium sulphate.

Figure 2.17 illustrates the effect of calcium sulphate on slump retention and how flash set occurs, due to the unregulated hydration of tricalcium aluminates, in the absence thereof.

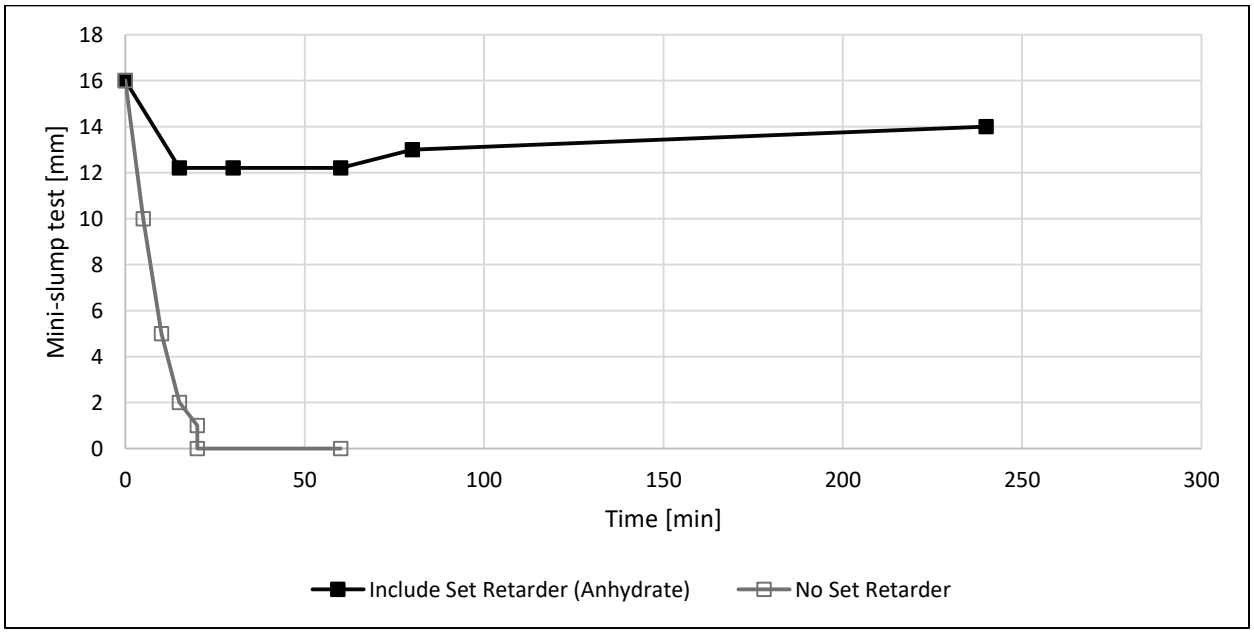


*Figure 2.17 Effect of set retarder on slump retention (after Prince, Espagne and Aïtcin, 2003)*

#### 2.6.1.2 Calcium sulphate – tricalcium aluminate – plasticiser/superplasticiser interaction

The reaction of tricalcium aluminates with calcium sulphate dominate the early stage hydration of cement. It is during this early stage hydration that superplasticisers interact with cement components. Normal hydration in cement mixes containing low concentration of dissolved sulphates are prohibited due to the superplasticiser reacting with tricalcium aluminates and preventing the formation of ettringite. This also occurs when the dissolution rate of calcium sulphates are low. The nature of the set retarder used is therefore as important as the dosage seeing that it determines its dissolution rate which in turn controls the rheology of the mix. From their study, Prince, Espagne and Aïtcin (2003) concluded that the dissolution of the set retarder is not only dependent on its nature but also depends on diffusion rate of sulphate ions. The study determined that superplasticisers cause a diffusion barrier at the solid-liquid interface of calcium sulphate therefore decreasing the rate of ettringite formation. This was supported in a study conducted by Rößler *et al.* (2007), where it was found that superplasticisers, in general, delay the dissolution of the calcium sulphate. This results in a low dissolved sulphate concentration in the cement solution. They found that PCE causes increased rate of $C_3A$ hydration by hindering the dissolution of hemihydrate whereas the use of SNF superplasticiser causes a decrease in both hemihydrate dissolution and $C_3A$ hydration. Therefore SNF does not significantly affect the hydration regulation of a cement. Superplasticisers containing sulphate function groups impair set retarder dissolution by increasing the sulphate concentration in the solution (Chakkamalayath *et al.*, 2011). Therefore it should be ensured that sufficient sulphate is available in the cement solution for reaction with $C_3A$. This can be controlled by using a set retarder with adequate solubility, dissolution rate and reactive sulphate.

The different components in cementitious materials have different charges i.e. $C_3S$ and $C_2S$ are anionic (negatively charged) whereas $C_3A$ and $C_3AF$ are positively charged. This causes superplasticisers, being negatively charged, to have an affinity for the two latter mentioned components. The presence of $C_3A$ therefore has a key influence on cement-plasticiser/superplasticiser compatibility due to its higher positive charge compared to other cement components. The influence of superplasticiser on the rheology of concrete is thus dependent on the availability of reactive $C_3A$, while the availability of reactive $C_3A$ is dependent on the amount of soluble sulphates. If cementitious materials contain high concentrations of $C_3A$,

with low quantities dissolved sulphates, superplasticiser will be absorbed readily and high slump loss is experienced (Chakkamalayath *et al.*, 2011).

The hydration products of $C_3A$ form layered double hydroxides (LDH):

$$2C_3A + 21H \rightarrow C_4AH_{13} + C_2AH_8 \rightarrow 2C_3AH_6 + 9H$$

These layered double hydroxides consist of positively charged outer layers with interlayer anions. The intermediate metastable hydration product of $C_3A$ i.e. $C_4AH_{13}$ and $C_2AH_8$ are particularly of interest. The interlayer of these LDH products consist of hydroxide anions. The presence of sulphates, generally in the form of dihydrate in OPC, within the concrete solution prevents the conversion of these products into $C_3AH_6$ by intercalating into the LDH. This results in the formation of ettringite and prevents flash set of a concrete mix. This is owing to sulphates being more negatively charged compared to hydroxides, therefore being more prone to intercalate into the LDH.

The presence of plasticiser/superplasticiser modifies the hydration of $C_3A$ by intercalating into the LDH, however this is undesirable since this results in less superplasticisers being available for dispersion of cement particles, inducing fluidity (Plank *et al.*, 2010). It is therefore important to understand when conditions are unfavourable for superplasticiser intercalation in order to avoid them.

When $C_3A$ hydrates in the absence of dissolved calcium sulphate, the interlayer is occupied by the plasticiser/superplasticiser in the mix solution owing to its negative charge being greater than that of hydroxide ions. This absorption of plasticiser/superplasticiser reduces the active dosage in the mix solution that can induce fluidity, thus reducing the efficiency of the plasticiser/superplasticiser. When $C_3A$ hydrates in the presence of both calcium sulphate and superplasticiser, the intercalation of superplasticiser into the LDH is heavily dependent on the concentration of sulphate in the mix solution. If low concentrations of sulphate is present, superplasticisers are still able to intercalate into LDH, the ability of superplasticiser to intercalate decreasing with increase in sulphate concentration. The interlayer is thus occupied by both sulphates and superplasticisers to achieve charge neutralization. If a sufficient concentration of sulphate is available in solution, superplasticisers will not be able to intercalate into the LDH due to the greater negative charge of sulphate ions causing it to have a greater affinity to occupy the

LDH. With the interlayer occupied by sulphate ions, $C_3A$ is converted to ettringite and the plasticiser/superplasticiser is adsorbed on the surface of the cement particle, resulting in electrostatic repulsion between particles. In concrete with high concentrations of sulphate it has been found that an anion exchange can occur between the sulphate and LDH with intercalated superplasticiser. The degree of exchange between superplasticiser and sulphate anion depends on the chemical composition of the superplasticiser. Figure 2.18 illustrates the interaction between superplasticiser and $C_3A$ in the presence of increasing sulphate concentration (Plank *et al.*, 2010).

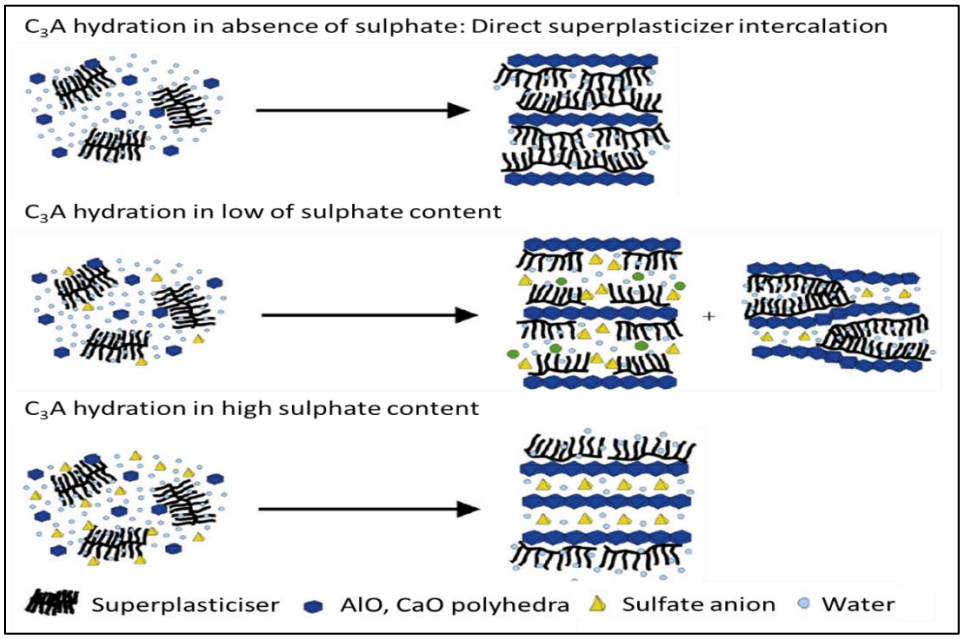


*Figure 2.18 Superplasticiser intercalation during $C_3A$ hydration at increasing levels of sulphate (after Plank et al., 2010)*

A mix containing both sulphate and superplasticiser thus follow the basic rule of intercalation: For a solution with various anions available the interlayer will be occupied by the anion with the highest negative charge, provided that the host layers are positively charged. Only once this source of anion is used up and non-neutralized host layers are still available, will less anionic molecules intercalate.

### 2.6.1.3 Tricalcium silicates

In cementitious materials containing low concentrations of $C_3A$, superplasticisers will react with and influence hydration of $C_3S$ and $C_2S$. The reaction between calcium sulphates and tricalcium aluminates has drawn great attention from researchers over the past years while neglecting the influence thereof on the hydration of tricalcium silicates. The effect of calcium sulphates on the

compressive strength gain, tricalcium silicates dominating the mechanical properties of cementitious materials, are thus a poorly understood topic. Gunay *et al.* (2011) conducted a study on the influence of calcium sulphates on the hydration of tricalcium silicates. They found that a change in $C_3A$-$CaSO_4$ reaction characteristics modifies the hydration of tricalcium silicate. It was found that the addition of calcium sulphates increased the early age (3 day) strength of concrete but had no effect on the long term (28 day) strength. This increase in early age strength was attributable to the increase in sulphate concentration within the mix solution resulting in an increased rate of hydration. The increased rate in hydration is due to the adsorption of calcium sulphate on the CSH surface modifying the nucleation product permeability. The morphology of CSH products are also altered to a finer needle structure that causes a denser matrix of interlocked hydration product. This results in a decrease in pore volume together with decrease in diameter of average pore size. It is well documented that the pore volume of concrete has a direct influence on strength (Zhang, Lin and Tong, 1996).

### 2.6.2 Influence of fineness

The fineness of cement has an impact on various early-age properties of the concrete such as setting time, workability and resistance against thermal cracking owing to its effect on the rate of hydration; the rate of hydration determining the heat evolution during hydration. A finer cement will exhibit more vigorous hydration between water and cement particles resulting in shorter setting times. Over the past decades the demand for finer cement has increased because of its ability to produce concrete with higher early age strength therefore shortening construction time. Finer cement allows for a desired target strength at lower cement content (Graham, Ballim and Kazirukanyo, 2011).

Hu, Ge and Wang (2014) used isothermal calorimetry test to study the influence of cement fineness on the early-age hydration of cementitious materials. Three cements with similar mineral and chemical composition but different fineness's were used. It was found that the hydration generated heat decreased with decreasing fineness. This is due to hydration taking place at the surface of cement particles, the surface area increasing with increasing fineness. This resulted in the finest cement having the shortest initial and final calorimetry setting time. Conversely, even though the coarsest cement had the lowest hydration rate, it was found to have the second shortest setting times. It is predicted that this phenomena is owing to the coarser cement requiring less hydration

to form a dense, interlocking structure of hydrated particles from the larger cement particles. Graham, Ballim and Kazirukanyo (2011) conducted similar studies and found a linear relationship exists between the surface area i.e. fineness of cement and hydration rate; the rate of hydration increasing with increased fineness, resulting in shorter setting time.

Furthermore, fine cement can be used to improve the rheology of a mix. This is achieved by improving the packing density of a cement via the use of fine cement and SCM, reducing the overall voids. Water needed to fill the voids are reduced and contribute to coating the solid particles, inducing fluidity. Chen and Kwan (2012) studied the influence of improved cement packing density on the rheology of concrete through the use of superfine cement as filler. Results indicated that the use of superfine cement as filler increases both flow rate and flow spread of cement due to the increased water film thickness around solid particles. However this was only true for w/c ratios below 0.22. Rheometer tests showed that a decrease in yield strength and plastic viscosity only occurs at a w/c ratio smaller than 0.22. A w/c ratio larger than 0.24 results in increased yield strength and plastic viscosity with the use of superfine cement even though the flow spread and flow rate still increased. A similar study was conducted by Mardani-Aghabaglou *et al.* (2017) on the influence of cement fineness on the rheology of cementitious materials in combination with PCE superplasticiser. The results obtained showed that setting time decreased with increasing cement fineness, as found in other studies discussed, irrespective of the PCE dosage. Furthermore, rheometer tests were conducted to determine the influence of cement fineness on the rheological parameters. Results showed that the rheological parameters were affected negatively with increase in cement fineness, causing an increase in plastic viscosity, static yield stress and dynamic yield stress, in the absence of superplasticiser. This could be due to the higher surface area of hydrating particles, causing an increase in water consumption. On the other hand, in the presence of superplasticiser the reverse was observed, the increase in cement fineness had a positive effect on cement rheology, causing a decrease in plastic viscosity, static yield stress and dynamic yield stress. It was concluded that superplasticiser adsorption on the surface of the cement particles increase with increased cement fineness, increasing superplasticizer effectiveness provided that adequate admixture dosage is used. However, the mix was more prone to segregation with increased cement fineness when superplasticiser was present.

The set retarder fineness also influences the hydration kinetics and rheology of concrete. It is well known that surface area increases with increasing fineness therefore also increasing the dissolution rate of a calcium sulphate used. Barbosa, Ramalho and Portella (2018) found that the rate of ettringite formation increases with increased gypsum fineness, via the use of calorimetry and X-ray diffraction. Furthermore, they investigated the effect that this has on the rheology of concrete using a Haake Rheostress rheometer. The use of finer gypsum influenced the rate of dissolution thus altering the hydration kinetics and causing increased rate of ettringite formation resulting in an increase in viscosity and yield stress.

### 2.6.3 Influence of supplementary cementitious materials

To keep up with the growing infrastructure needs the need for new construction materials in the building sector is in constant demand. One of the prevailing problems with cement manufacturing is the amount of $CO_2$ produced. The use of SCM such as fly ash (FA), silica fumes (SF) and slag (SL) is used to produce a greener, environmentally friendly cement. Furthermore, the use of SCM can enhance aesthetical and hardened state properties as well as grain size distribution. However, SCM also have an influence on the hydration kinetics and rheology of cementitious materials and it is therefore necessary to study the compatibility of SCM with other cement components, additives and admixtures.

Fly ash, a reactive pozzolanic material, is produced as a by-product during coal combustion and graded from Class C to Class F depending on the calcium content, the calcium content increasing from Class C to Class F. The higher the calcium content of a FA the more efficient cement substitute it becomes by contributing to concrete strength through undergoing hydration. The use of FA as cement replacement in small quantities is also known to improve rheological properties due to the larger particle size and spherical shape. Ng and Justnes (2016) investigated the compatibility of superplasticizer with cement containing high percentages (20-60%) of Class F fly ash using rheometer and calorimeter tests. From their studies it was found that the addition of fly ash increases initial flow. However setting is delayed due to the FA being less reactive than cement and containing inert particles. Furthermore, it was found that superplasticiser has a greater affinity towards cement particles than towards FA. Thus when a percentage of the binder is replaced with up to 60 % FA the active superplasticiser to cement ratio increases, hence allowing more superplasticiser to be adsorbed onto the surface of cement particles, causing particle dispersion.

This also causes cement containing high percentages of fly ash to be more prone to segregation with the addition of superplasticizer. The use of low percentages of fly ash has negligible effect on superplasticiser adsorption. Robert, Sathyan and Anand (2018) investigated the influence of superplasticisers on the rheology of cement containing ultrafine fly ash. From their studies it was found that the use of ultrafine fly ash increases yield strength and plastic viscosity at constant admixture dosage. It can therefore be deducted that the effect of FA on the immediate rheology of cementitious material is depended on the particle size and quantity whereas the class of FA used determines the effect on rheology over time.

Another material used as cement substitute is slag. Slag is a by-product produced from raw iron ore processing. The use of slag as SCM reduces cement cost and its negative impact on the environment. Slag as SCM has various advantages for instance higher acid and sulphate resistance, improved workability, better corrosion resistance and less hydration heat generation, the extent depending on the chemical composition and fineness of the slag used. The shape and roughness of slag particles depend on the milling process for example rough angular shaped slag particles are obtained using a ball-mill whereas a smooth spherical particle shape is obtained using a vibro-mill (Rashad, 2018). Although the chemical composition of slag is similar to that of cement it is less reactive and could therefore cause set delay when used in high quantities. Boukendakdji *et al.* (2009) found that the use of Algerian slag, having a fineness higher than that of cement, increases the fluidity of a mix by decreasing the water demand. Slump flow increased with up to 20% cement substitution with slag after which the viscosity and yield stress increased. The period for which workability was maintained increased with increased slag substitution. It was concluded that this is due to the slag being less reactive than cement. However, Ting, Qiang and Shiyu (2019) have found that the effect of slag on the initial setting time is dependent on both the dosage and fineness. Ultrafine slag having a higher rate of hydration than cement, causing earlier mix stiffening.

The use of silica fumes, a by-product of ferrosilicon production, as SCM started as a result of air pollution regulations. Studies conducted on the material, SF dominantly consisting of free silica, showed that it could be used as a reactive pozzolanic material. This together with the large surface area of SF makes it very reactive. The use of SF does have some disadvantages such as its high price. SF consist of fine particles that enhance cement packing density, thus acting as a filler that effect the early stages of hydration by contributing to CSH formation, improving early age strength

and durability of concrete by decreasing porosity. However, SF are known to agglomerate at high dosages due to the strong Van der Waals forces between particles, reducing the surface exposed for reaction, causing lower contribution to hydration. SF also influence the rheology of concrete. Like cement particles, SF has a positive surface charge causing negatively charged superplasticiser to adsorb to the surface of SF particles and contribute to the dispersion of particles. Due to the SF providing additional surface area for superplasticiser adsorption the negative retarding effect of superplasticisers on cement hydration can be reduced by the use thereof. However, the adsorption of superplasticizer on the surface of SF particles block nucleation sites and decrease its contribution to hydration (Berntsson, 1996). Meng, Kumar and Khayat (2019) found that the partial substitution of cement with SF enhances the hydration rate therefore shortening the setting time, this effect decreasing with increase SF used. Furthermore, they found that the use of SF increases yields strength and plastic viscosity because of the fineness of SF increasing packing density and water demand, this effect decreased with the increase in superplasticiser dosage.

### 2.6.4 Concluding Summary

The literature review provides background on the importance of cement production to the construction industry. It is noted that the heat generated during the milling of clinker and calcium sulphate, to produce cement, might cause peaks in temperature at localised areas within the mil. These increased temperatures could result in the dehydration of calcium sulphate dihydrate to hemihydrate and to a lesser extent, anhydrite.

It is discussed how the presence of different types of calcium sulphate in cement may cause unpredictable concrete performance. This problem being emphasised by the use of plasticiser/superplasticiser chemical admixtures, as is done frequently in modern concrete design. This is due to both plasticiser/superplasticiser and calcium sulphate having an affinity for the aluminate phase in cement that dominate the fresh state properties of concrete.

Subsequently, the influence of this interaction on the fresh state properties and hydration of concrete is discussed. The use of rheology to quantify the fresh state properties and structuration of concrete is discussed in detail. The use of rheology to assist with the identification of compatibility issues between plasticiser/superplasticiser and different types of calcium sulphate are emphasised; the link between rheological parameters and practical aspects such as segregation resistance, formwork pressure, surface finish quality and pumping pressure being made.

Finally, a brief overview on the influence of calcium sulphate on the compressive strength gain, tricalcium silicates dominating the strength gain of cementitious materials, is provided. This is followed by a short discussion of other factors which influence concrete performance, in particular, cement fineness and SCM's, and possible causes of unpredictable concrete behaviour.

The literature review validates the necessity for further investigation on the influence of plasticiser/superplasticiser to calcium sulphate interaction on concrete performance.

The subsequent chapter provides insight on the experimental framework of this study.

# Chapter 3: Experimental framework

This chapter provides a discussion on the materials used, including aggregate, cement, mineral and chemical admixtures and insight on the mix design process is provided. An overview of the test programme developed to quantify the influence of calcium sulphate to plasticiser/superplasticiser interaction on the fresh state properties and hydration of concrete is provided. Finally, the tests performed are discussed in detail with emphasis placed on the test methodologies and parameters obtained from each test.

## 3.1 Materials and mix design

The rheology of concrete is influenced by almost all aspects of the mix design, including w/c ratio, fines content, aggregate properties, aggregate surface texture and angularity, gradation, chemical and mineral admixtures (Ferraris et al., 2017). It was therefore ensured that all aspects of the mix design was kept constant to ensure that the rheological parameters of a mix were only influenced by the chemical and mineral admixture under consideration.

## 3.2 Aggregate

Fine natural quarry sand, locally known as Malmesbury sand and produced from the natural weathering of rock, was used in all mix designs as a result of its grading as seen in Figure 3.1. The grading of aggregate was determined in accordance with SANS 1083:2017 (SANS, 2017).

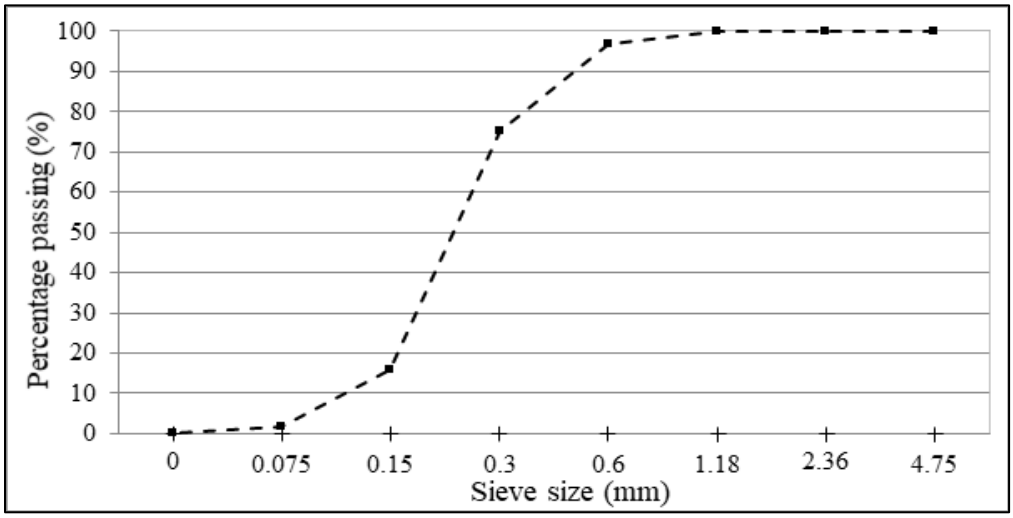


*Figure 3.1 Fine Malmesbury sand particle size distribution*

Greywacke stone, produced from the crushing of Malmesbury shale, with a 6 mm nominal stone size was used for all mixes. These aggregate consist of inert particles, the cement / mineral admixture therefore being the only source of thixotropy within the mix. Aggregate properties are presented in Table 3.1.

*Table 3.1 Aggregate properties*

| Aggregate | Relative density [kg/m^3] | Fineness Modulus |
|---|---|---|
| Fine natural quarry Sand | 2.58 | 1.12 |
| 6 mm Greywacke stone | 2.68 | - |

### 3.2.1 Cement and calcium sulphate

A CEM I 52.5N, supplied by PPC (Pretoria Portland Cement Co. Ltd.), was used for all mixes. The major chemical composition of the cement, obtained from X-Ray Fluorescence (XRF) analysis is presented in Table 3.2. Bogue's equations were used to determine the percentages $C_3A$, $C_4AF$, $C_3S$ and $C_2S$ (Domone and Illston, 2010).

*Table 3.2 Cement composition*

| Cement composition | Percentage [%] |
|---|---|
| Clinker | 92,69 |
| Gypsum | 3,80 |
| Lime | 3,50 |
| Other | 0,01 |
| Total | 100 |
| $Al_2O_3$ | 3,90 |
| CaO | 64,54 |
| $Fe_2O_3$ | 2,94 |
| $K_2O$ | 0,59 |
| $Na_2O$ | 0,20 |
| $P_2O_5$ | 0,16 |
| $SiO_2$ | 20,24 |
| $TiO_2$ | 0,22 |
| $S0_3$ | 4,47 |
| L.O.I. | 2,73 |
| Total | 100 |
| $C_3A$ | 5,4 |
| $C_4AF$ | 8,9 |
| $C_3S$ | 65,7 |
| $C_2S$ | 8,6 |

*L.O.I = Loss on ignition at 1000℃

The dihydrate (gypsum) and hemihydrate (basanite), supplied by PPC, used during testing has a major chemical composition, obtained from XRF analysis, as presented in Table 3.3.

*Table 3.3 Chemical composition of dihydrate and hemihydrate*

| | Concentration | | |
|---|---|---|---|
| **Compound** | **Dihydrate** | **Hemihydrate** | **Unit** |
| **$SO_3$** | 52,9 | 54 | % |
| **CaO** | 44,6 | 43,4 | % |
| **$SiO_2$** | 1,15 | 0,824 | % |
| **MgO** | 0,628 | 0,85 | % |
| **$Fe_2O_3$** | 0,33 | 0,161 | % |
| **$Al_2O_3$** | 0,181 | 0,175 | % |
| **SrO** | 0,164 | 0,563 | % |
| **$K_2O$** | 441 | 92 | ppm |
| **$Cr_2O_3$** | 87 | 94 | ppm |

Table 3.4 presents the Blaine fineness of the cement and calcium sulphate used, as determined in accordance with SANS 50196-6:2014 (SANS, 2014). The dihydrate used during tests was also dehydrated, at various temperatures typically experienced during milling, for 24 hours to determine how the dehydration of dihydrate to hemihydrate influences Blaine fineness. From Table 3.4 it is evident that the dehydration of dihydrate to hemihydrate causes a corresponding increase in particle surface area. A similar increase in dihydrate particle surface area, during dehydration, was found by Strydom and Potgieter (1999). From the study Strydom and Potgieter (1999) concluded that the change in dihydrate surface area, during dehydration, is a function of both temperature and time of exposure to increased temperatures; the surface area increasing as the time exposed at elevated temperatures increase.

*Table 3.4 Cement and calcium sulphate Blaine fineness*

| Material | Blaine fineness [cm2/g] |
|---|---|
| Cement | 4740 |
| Dihydrate (Obtained from PPC) | 4930 |
| Dihydrate dehydrated to hemihydrate at: | |
| 110℃ | 5860 |
| 120℃ | 6120 |
| 130℃ | 6340 |
| Hemihydrate (Obtained from PPC) | 6430 |
| 140℃ | 6450 |
| 150℃ | 6710 |

### 3.2.2 Admixtures

Chryso SA (Pty) Ltd. chemical admixtures were used during the study. The following admixture descriptions were obtained from the supplier's general catalogue Chryso SA (2007):

- Chryso Plast 900 is a modified lignosulphonate water reducer that has been selected for its quality, performance and consistency. Chryso Plast 900 can be used with or without mineral admixtures and has a strong dispersant action therefore permitting concrete fluidizing while maintaining low w/c ratios.
- Chryso Fluid L is a sulphonate naphthalene formaldehyde based superplasticiser used for high water reductions while maintaining mix consistency or inducing high fluidity at constant w/c ratios.
- Chryso Fluid Premia 310 is a modern modified polycarboxylate polymer based superplasticiser. Chryso Fluid Premia 310 is specifically applicable for use in SCC.

Recommended admixture dosages, as per supplier, are presented in Table 3.5.

*Table 3.5 Recommended plasticiser/superplasticiser dosages as per supplier*

| Type | Brand Name | Recommended dosage [litre/100kg of cementitious content] | |
|---|---|---|---|
| | | Min | Max |
| LS | Chryso Plast 900 | 0,2 | 0,5 |
| SNF | Chryso Fluid L | 0,6 | 2 |
| PCE | Chryso Fluid Premia 310 | 0,3 | 3 |

### 3.2.3 Mix design

A w/c ratio of 0.45 was chosen and kept constant for all mixes. It was opted to use this w/c ratio as it would allow sufficient water to hydrate all the cement particles and fill the resulting pores (Domone and Illston, 2010). The reference mix was designed with high fluidity, having a true slump of 200 mm (close to the maximum slump allowed by BS EN 12350-2, 2019). This was to ensure that the mix would maintain a slump larger than 75 mm for the entire testing period, specified as a prerequisite for the use of the ICAR Rheometer, despite alterations being made to the mix. The result was a mix that was robust and showed no signs of segregation when alteration were made. Mix proportions are presented in Table 3.6.

*Table 3.6 Reference mix proportions*

| | **Reference Mix** | | |
|---|---|---|---|
| | **Mass (kg/m$^3$)** | **RD** | **Volume (Liter)** |
| Water | 237 | 1,00 | 237 |
| Cement | 526 | 3,14 | 167 |
| Stone | 760 | 2,68 | 284 |
| Sand | 806 | 2,58 | 312 |
| Total | | | 1000 |

#### 3.2.3.1 Mixes containing chemical admixture

With a reference mix obtained, as described in Section 3.2.3, one plasticiser and two superplasticisers were used to increase the workability of the mix while maintaining a constant w/c ratio. By keeping the w/c ratio constant the performance of each chemical admixture was examined by considering the ability to increase fluidity. Chemical admixtures were introduced into the mix by adding it to the water. This was done to ensure that all chemical admixtures are introduce to the mix at the same concrete age i.e. when hydration starts. The chemical admixtures used were as described in Section 3.2.2. The performance of each chemical admixture was evaluated at two dosages i.e. at minimum and twice the minimum supplier suggested dosage (both dosages being lower than the optimal dosage of each plasticiser/superplasticiser for the specific mix design) as presented in Table 3.5. To ensure that the dosages used were lower than the optimum dosage, the reference mix was modified with more than twice the minimum supplier suggested plasticiser/superplasticiser dosage and a slump test was performed. Since this study aims to identify compatibility issues that arise from improper chemical-mineral admixture combinations it was opted not to test at optimal dosage of the respective chemical admixtures. The optimal

dosage is determined by incrementally increasing the dosage of admixture until no further change in fluidity is measured, usually in terms of slump. Thus at the optimal dosage the mix would be very sensitive to alterations which is not desirable for this study.

#### 3.2.3.2 Mixes containing additional calcium sulphate

To evaluate the influence of the type of calcium sulphate on the fresh state properties and hydration of concrete, the reference mix was modified through the addition of dihydrate and hemihydrate, respectively. Additions at two different percentages were applied i.e. 2% and 4% addition. However, to ensure that the binder content (consisting of both calcium sulphate and clinker) remained constant substitution was used to increase the calcium sulphate within the selected percentage. The addition of calcium sulphate without keeping the binder content constant will increase the water demand of the mix through the addition of fines. The binder content is therefore kept constant to ensure that the result of respective addition of dihydrate and hemihydrate, in terms of loss of workability, is due to the type of calcium sulphate.

#### 3.2.3.3 Mix terminology

Nomenclature was developed to distinguish between mixes with different constituents. This is to easily deduce the type of calcium sulphate and chemical admixture used to augment the reference mix. Furthermore, the percentage of calcium sulphate and dosage of chemical admixture can easily be deducted from the mix denotation. Figure 3.2 explains the nomenclature developed to describe the respective mixes as used throughout this study.

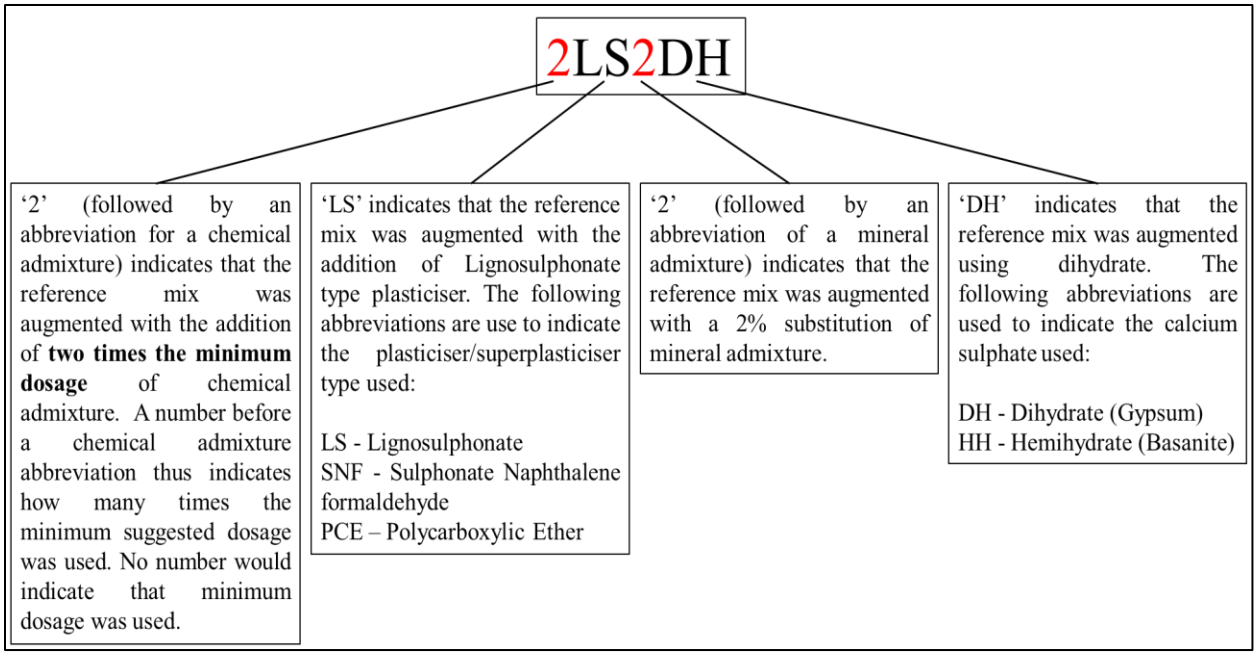


*Figure 3.2 Nomenclature for mixes*

## 3.3 Test programme

Various mixes were designed to determine the influence of cement composition (cement containing various types of calcium sulphate) on the performance of plasticisers / superplasticiser and how this influences the fresh state properties and hydration of concrete. To limit the effect of external factors on results and ensure that the results obtained reflect the influence of the set retarder / admixture under investigation, various quality control measures were taken. All aggregate, cement and mineral admixtures were stored in a climate controlled room, at 23± 2° C and 65% relative humidity, for at least 12 hours before use. Furthermore temperature sensitive tests were performed in the aforementioned climate controlled room. The curing of samples used for time dependent tests were performed in accordance with SANS 5861-3:2006 (SANS, 2006b). Samples used for rheometer tests were thus covered with a damp cloth during periods of zero shear. Table 3.7 provides a test programme while Section 3.4 provides information regarding the test procedures.

*Table 3.7 Test programme*

| Test | Quantity | Parameters obtained | Tests performed per data point |
|---|---|---|---|
| Solubility tests | 24 | Solubility [$CaSO_4$g / 100g water] | 3 |
| Hydration temperature development tests | 36 | Temperature development curve | 3 |
| Slump / slump flow test | 69 | Slump / slump flow [mm] | 3 |
| ICAR Rheometer tests: | | | |
| Flow Curve test | 23 | Plastic viscosity [Pa.s] | 1 |
| Stress Growth test | 138 | Static Yield Stress [Pa] | 1 |
| | | Dynamic Yield Stress [Pa] | 1 |
| | | Rate of structuration [Pa/min] | 5 |
| Vicat Setting time test | 69 | Initial setting time [min] | 3 |
| Cube Compression test | 207 | 1, 3 and 7 day cube compressive strength [MPa] | 3 |

## 3.4 Test procedure

Since the rheological properties of cementitious materials are dependent on the age of the material, hydration starting as soon as water is made available, the test procedure for rheological and cube compression tests were followed as presented in Table 3.8

*Table 3.8 Test program followed to determine parameters*

| Start time | Time at rest | Duration | Activity | Obtained |
|---|---|---|---|---|
| - | - | Mix dry aggregate for 1 minute | Mix dry constituents | - |
| (Time since water with chemical admixture is added) 00:00:00 | - | 2 min | Add water and mix concrete (2min in total) | - |
| 00:02:00 | - | 3 min | Slump / Slump flow test | Slump / Slump flow |
| 00:05:00 | - | 2 min | Load rheometer bucket with concrete and set up test | - |
| 00:07:00 | 0 s (initial test) | 60 s | Flow curve test | Plastic viscosity |
| 00:08:00 | 1 min | 60 s | Stress growth test | Initial SYS and DYS |
| 00:10:00 | 5 min | 60 s | Stress growth test | Obtain SYS to determine $A_{thix}$ |
| 00:16:00 | 10 min | 60 s | Stress growth test | Obtain SYS to determine $A_{thix}$ |
| 00:27:00 | 20 min | 60 s | Stress growth test | Obtain SYS to determine $A_{thix}$ |
| 00:48:00 | 40 min | 60 s | Stress growth test | Obtain SYS to determine $A_{thix}$ |
| 01:29:00 | 60 min | 60 s | Stress growth test | Obtain SYS to determine $A_{thix}$ |
| - | 1 day | - | Cube compression test | Compressive strength |
| - | 3 day | - | Cube compression test | Compressive strength |
| - | 7 day | - | Cube compression test | Compressive strength |

This test program was followed strictly to ensure that the test data obtained were comparable at all time intervals. All mixes were mixed (dry and wet) for 3 minutes in total, a slump or slump flow test following directly afterwards. The rheometer bucket was then loaded with at least 19 litres of concrete, ensuring that the vanes were submerged in concrete. A flow curve test was then performed to obtain the plastic viscosity of each mix after which six stress growth tests were performed. The first stress growth test is performed to obtain the initial rheological properties of

each mix whereas the five following stress growth tests are used to determine the rate of structuration. Incremental periods of rest i.e. 5 min, 10 min, 20 min, 40 min and 60 min, were allowed between each stress growth test during which mixes lose fluidity due to structuration on a microscopic level and gain strength in the liquid state. All stress growth tests used to determine a rate of structuration were performed on the same mix of concrete. This was deemed to be acceptable since the chemical reactants responsible for the structuration of concrete are not depleted during the testing period. Vicat initial setting time tests were also conducted for all mixes. Furthermore, cubes were cast which were later used to determine the compression strength at 1, 3 and 7 days. To determine the influence of plasticiser/superplasticiser on the solubility of calcium sulphate simple solubility test were conducted. Furthermore, the influence of the type of calcium sulphate and the calcium sulphate-plasticiser/superplasticiser interaction on the rate of hydration was investigated by measuring the heat generated during hydration over a period of 7 days.

### 3.4.1 Solubility test

Solubility tests were conducted to determine the difference in solubility of dihydrate and hemihydrate as well as to determine how the presence of various plasticiser/superplasticisers influence the solubility of the calcium sulphate under consideration. The solubility test methodology, as described by Bock (1961) was adopted. Pure osmosis filtered water was saturated with a known amount of dihydrate and hemihydrate. To determine the influence of plasticiser/superplasticiser on the solubility of calcium sulphate the water solution was modified via the addition of plasticiser/superplasticiser while keeping the amount of calcium sulphate (2 g) added to the solution constant. The water to plasticiser/superplasticiser ratio was kept in accordance with the plasticiser/superplasticiser manufacturer specifications. Solubility cells were thus filled with 150 ml water and modified via the addition of twice the minimum manufacturer suggested dosage of plasticiser/superplasticiser. 1.33 ml LS plasticiser, 4 ml SNF – and 2 ml PCE superplasticiser were thus added to 150 ml of water in the solubility cells. Solubility cells were then placed in a water bath, kept at a temperature of 23±0.5℃, until the temperature of all the solutions stabilised at the set temperature as seen in Figure 3.3. Using an analytical balance, a pre-weighed amount of dihydrate and hemihydrate was added to the solubility cells and stirred at a constant rate using a magnetic stirrer for 150 min. This period was chosen as it concurs with the maximum time lapsed during ICAR Rheometer tests. Once the solutions were stirred for the set time, excess solids were extracted from the solution via filtration through a 0.45 µm filter paper

placed in a glass filter connected to a suction flask (presented in Figure 3.3) to accelerate the filtration process. The weight of each filter paper was obtained in advance using an analytical balance, accurate to 0.001 g. The filter papers, containing the excess solids were then placed into a vacuum oven at 105℃ for 24 hours to ensure that all moisture is removed from the samples. The dry mass of the filter paper with excess solids were then obtained using an analytic balance, and the solubility of each solution calculated.

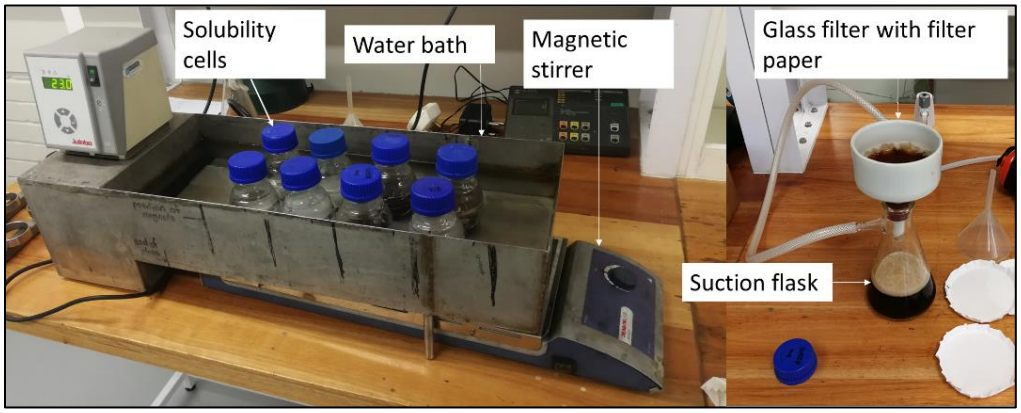


*Figure 3.3 Solubility test equipment*

## 3.4.2 Hydration temperature tests

The temperature generated during hydration was monitored to determine the influence that the type of calcium sulphate, as well as the relation between calcium sulphate and plasticiser/superplasticiser has on the rate of hydration. Vishay NTC Thermistors 10 kΩ with measurement range from 0 – 50°C and accurate to three decimal places were used to measure the temperature change of a 100x100x100 mm cube until a concrete age of seven days. However, it was found that after three days no further significant change in temperature is measured by the thermistors. Thermistors were fixed to a T-section and inserted into the centre of the cube at a depth of 50 mm, as seen in Figure 3.4. To ensure that all tests start from the same temperature all materials and equipment were stored in a climate control room for at least 24 hours before use. Tests were performed in the same aforementioned climate control room and cubes were placed in a polystyrene box to limit the heat loss. Three cubes were tested per mix.

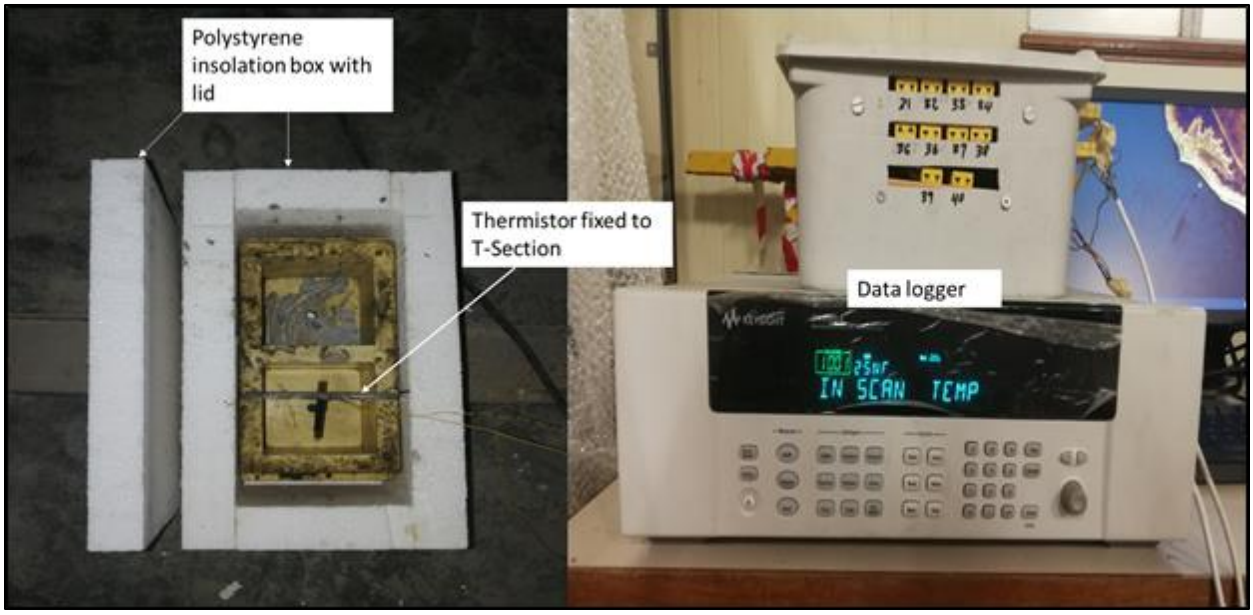


*Figure 3.4 Hydration temperature test equipment.*

### 3.4.3 Slump or slump flow test

Directly after a concrete mix was completed a slump or slump flow test, depending on the mix fluidity, was performed in accordance with BS EN 12350-2:2019 (BS EN, 2019) and BS EN 12350-8:2019 (BS EN, 2019), respectively. Using apparatus that conform to standards, as presented in Figure 3.5, a slump test was conducted by filling the mould in three layers, making sure to tamp each layer. With the slump cone filled, concrete extruding the mould is scrapped off and the mould is slowly lifted without any torsional or lateral movement. Directly after demoulding the slump is measured as the difference between the height of the cone and the concrete slump height, measured to the highest point. The slump flow tests follow a similar methodology, however the slump flow is measured as the average diameter, measured in two perpendicular directions. The slump or slump flow is used to give an indication of the workability and cohesion of a mix in conjunction with rheological parameters.

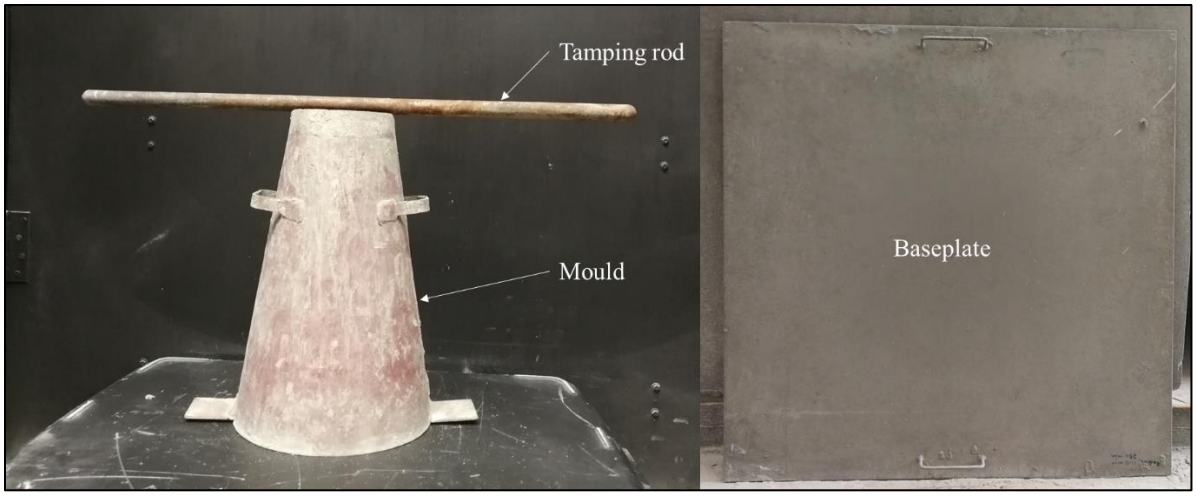


*Figure 3.5 Slump and slump flow apparatus*

### 3.4.4 ICAR rheometer tests

The Germann Instruments produced ICAR Rheometer was used to determine rheological parameters such as the plastic viscosity, static - , dynamic yield stress, thixotropy and rate of structuration. The ICAR Rheometer consists of a motor, four blade vane with 63.5 mm diameter and 127 mm depth, frame on which the motor rests during testing and a 20 litre container with outer radius of 143 mm and vertical strips to ensure that no slip occurs between the specimen and container wall (as presented in Figure 3.6).

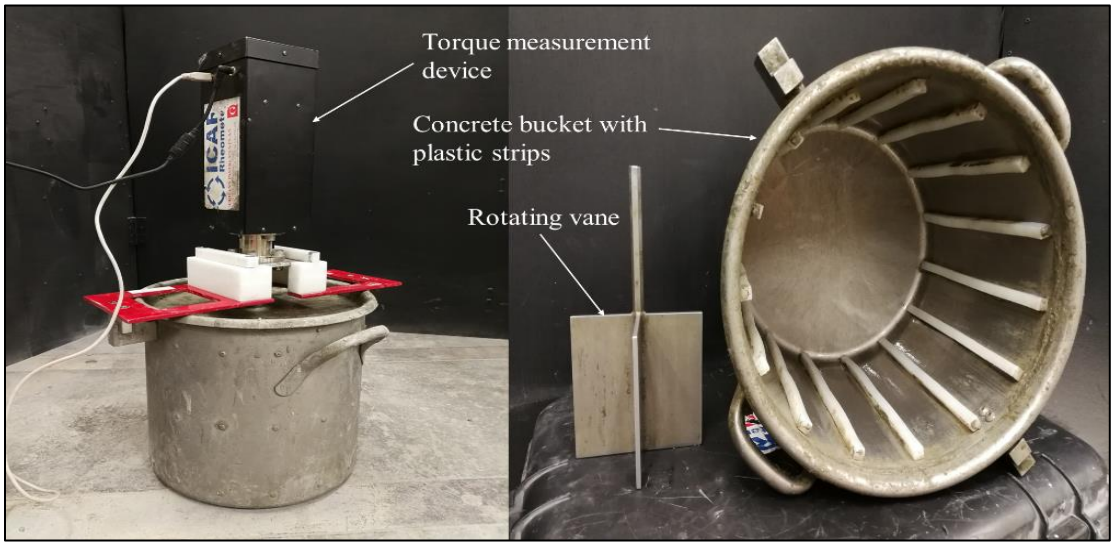


*Figure 3.6 ICAR Rheometer*

Two test can be performed using the ICAR Rheometer i.e. the flow curve and stress growth test, where each test follows the same procedure of filling the container with 19 litres of concrete, positioning the vane inside the concrete mix, choosing the input parameters for the software and performing the test. Upon completion of the test the container is emptied; examining the specimen to determine whether any segregation has occurred during testing.

#### 3.4.4.1 Flow curve test

The flow curve test was performed to obtain the Bingham parameters i.e. plastic viscosity and dynamic yield stress. Before a flow curve test is performed the concrete mix was pre-sheared to ensure that each specimen is tested from the same destructured state. The flow curve test follows immediately after pre-shear. The test is performed by shearing the concrete mix at incrementally smaller shear rates and measuring the corresponding dynamic yield stress. The ICAR Rheometer software input parameters are presented in Table 3.9. The rheometer software automatically divides the difference between the input initial and final speed into equal increments of shear rate according to the number of points requested.

*Table 3.9 Input parameters for flow curve test*

| **Flow curve test input parameters** | | |
|---|---|---|
| Breakdown speed | 0.2 | rps |
| Breakdown Time | 25 | s |
| Number of points | 7 | |
| Time per point | 5 | s |
| Initial speed | 0.2 | rps |
| Final speed | 0.05 | rps |

The rheometer measures the rotational speed of the vane as well as the torque acting on the vane. ICAR Rheometer software uses the Reiner-Riwlin equation, presented by Equation 3.1, to calculate the yield stress and plastic viscosity based on the Bingham model as defined in Section 2.2 (Germann Instruments A/S, 2016).

$$\Omega = \frac{T}{4\pi h\mu}\left(\frac{1}{R_1^2} - \frac{1}{R_2^2}\right) - \frac{\tau_0}{\mu}\ln\left(\frac{R_2}{R_1}\right) \qquad 3.1$$

Where:

$$\Omega = rotation\ speed\ \left[\frac{rad}{s}\right]$$

$T = torque\ [Nm]$

h = vane height [m]

$R_1 = vane\ radius\ [m]$

$R_2 = outer\ radius\ of\ container\ [m]$

Should the specimen not shear homogeneously and a region of zero flow is identified by the user the modified Reiner-Riwler equation, presented by Equation 3.2, should be used. The region of zero flow/shear can be calculated using Equation 3.3.

$$\Omega = \frac{T}{4\Pi h\mu}\left(\frac{1}{R_1^2} - \frac{2\pi h\tau_0}{T}\right) - \frac{\tau_0}{2\mu}\ln\left(\frac{T}{2\pi h\tau_0 R_1^2}\right) \quad 3.2$$

$$R_{2,eff} = \sqrt{\frac{T}{2\pi h\tau_0}} \quad 3.3$$

### 3.4.4.2 Stress growth test

The stress growth test is performed to obtain the static yield stress and characterise the thixotropic behaviour of the specimen. Although concrete generally experiences much larger shear rates during the construction process, an input shear rate of 1 $m.s^{-1}/m$, calculated to be equal to 0.2 rps for the specific vane and container size, using Equation 3.4 for the ICAR Rheometer used, was applied to each specimen due to the limitation on the maximum rotational speed of the ICAR Rheometer (Germann Instruments A/S, 2016).

$$\dot{\gamma} = \frac{rps \cdot r_i \cdot 2\pi}{(r_o - r_i)} \quad 3.4$$

Where:

$r_i = vane\ radius\ [mm]$

$r_o = bucket\ radius\ [mm]$

During the stress growth test the vane rotates at a constant angular velocity, 0.2 rps, and the change in torque is recorded. Once the test is initiated the torque is monitored until a peak, associated with the static yield stress is observed. Thereafter the specimen is left to shear at the constant speed until no further fluctuation in torque is observed, which in this study occurred around 60 s into the test. Tests were therefore stopped after 60 s of run time after which the lowest torque measured within the 60 s period was used to calculate the dynamic yield stress. The ICAR rheometer

software records the maximum torque during a test and calculates the static yield stress using Equation 3.5 (Germann Instruments A/S, 2016). The dynamic yield stress however is calculated manually with Equation 3.5 using the lowest torque measured during the 60 s shearing time. It was ensured that each specimen shears homogeneously at the input rotational speed.

$$\tau_0 = \frac{2T}{\pi D^3 \left(\frac{H}{D} + \frac{1}{3}\right)} \qquad 3.5$$

Where:

D = vane diameter [m]

H = vane height [m]

Thixotropic behaviour of cementitious materials can be divided into two aspects, the flocculation and structuration when at rest. Where the measurement of the latter is more applicable to practical applications than the first as it is the rate of structuration of cementitious materials that influences the stability of the specimen. To characterise the rate of structuration of the specimen in study, Kruger's bi-linear thixotropic model was adopted. This model describes a rate of re-flocculation, $R_{thix}$, as well as a rate of structuration, $A_{thix}$. Both parameters are measured as the increase in static yield stress over time and assumes a bi-linear increase in SYS at rest. Kruger's model, as seen in Figure 3.7, can be described using the following equations (Kruger, Zeranka and Zijl, 2019):

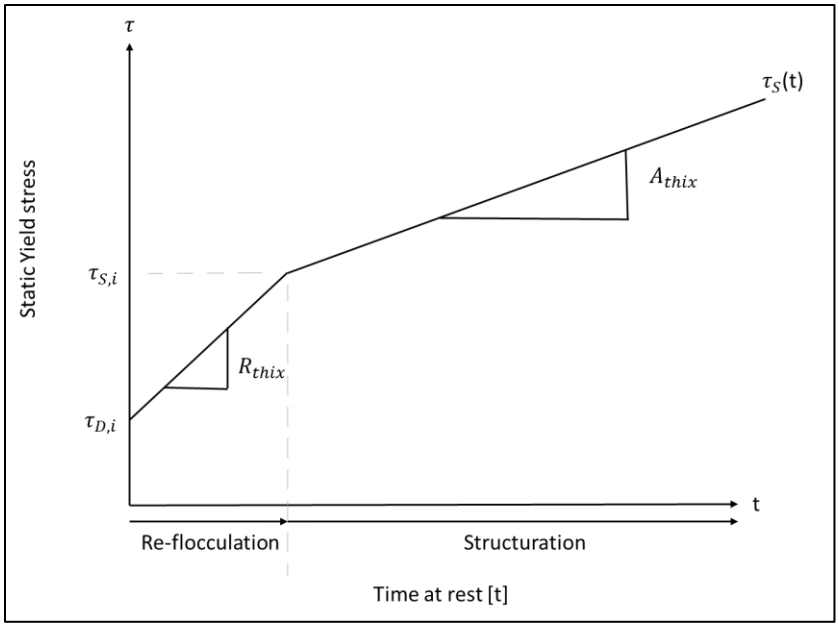


*Figure 3.7 Kruger's thixotropic model*

For the period of re-flocculation;

$$\tau_S(t) = R_{thix} \cdot t + \tau_{D,i} \quad 3.6$$

Where:

$\tau_S(t) = SYS\ after\ time\ t\ of\ zero\ shear\ [Pa]$

$R_{thix} = Rate\ of\ re-flocculation\ \left[\frac{Pa}{s}\right]$

$t = time\ without\ any\ agitation/shear\ [s]\ (t < t_{rf})$

$\tau_{D,i} = initial\ DYS\ from\ fisrt\ stress\ growth\ test\ [Pa]$

It should be noted that $t$, the time without any agitation, has to be smaller than $t_{rf}$, the time of re-flocculation for Equation 3.7 to be valid:

$$t_{rf} = \frac{\tau_{S,i} - \tau_{D,i}}{R_{thix}} \quad 3.7$$

Where:

$\tau_{S,i} = initial\ SYS\ from\ first\ stress\ growth\ test\ [Pa]$

For the period of structuration;

$$\tau_S(t) = A_{thix} \cdot t + \tau_{S,i} \quad 3.8$$

Where:

$\tau_S(t) = SYS\ after\ time\ t\ of\ zero\ shear\ [Pa]$

$A_{thix} = Rate\ of\ structuration\ \left[\frac{Pa}{s}\right]$

$t = time\ without\ any\ agitation/shear\ [s]\ (t > t_{rf})$

$\tau_i = initial\ yield\ stress\ [Pa]$

To determine $A_{thix}$ of a specimen, various stress growth tests were performed at incremental periods of rest i.e. zero shear. Periods of rest consisting of 5, 10, 20, 40 and 60 minutes were used in between tests. However, before tests could be performed a reference state had to be defined to ensure that all concrete mixes were tested from the same destructured state. The reference state is defined as the most deflocculated state which coincides with the point in time that the specimen experienced the highest shear rate. The reference state was achieved during the flow curve test by pre-shearing each concrete mix once at a rotational speed of 0.2 rps for 25 seconds. The first stress growth test was immediately performed once the flow curve test was completed.

### 3.4.5 Vicat initial setting time test

The Vicat apparatus (as seen in Figure 3.8) and the procedure used to determine the initial setting time of each respective mix is as set out in SANS 50196-3:2006 (SANS, 2006a). The initial setting time is defined as the time elapsed from ‘zero time’ until the needle penetrates into the sample a distance of 6 ± 3 mm from the baseplate on which the specimen is placed. The penetration of the 1.1mm needle was measured at intervals of 10 minutes until resistance was observed after which 5 minute intervals were adopted. Although this test was intended for pastes at standard consistency a mortar was used. The obtained initial setting time therefore only serves as an indication of when the mix loses workability. The mortar was obtained by vibrating the concrete mix over a 4.75 mm sieve, thus separating out the stone. Thereafter the mould was filled with the mortar and the test was performed.

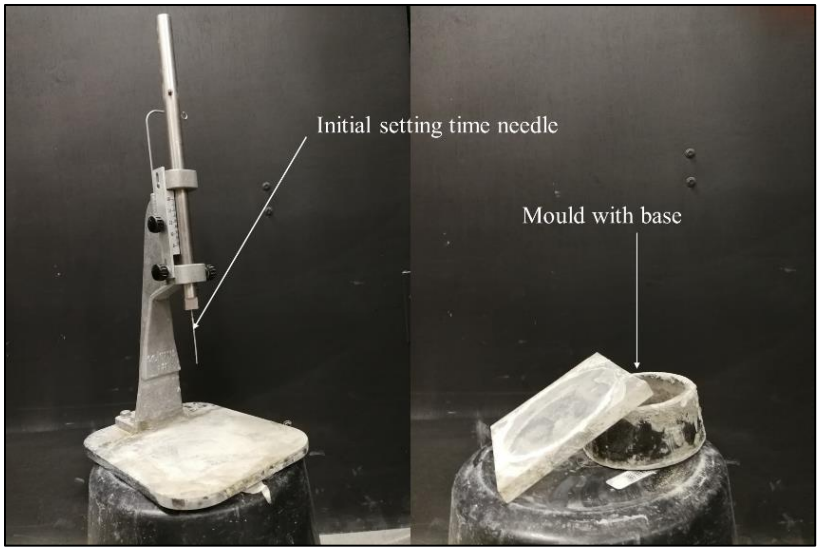


*Figure 3.8 Vicat setting time apparatus*

### 3.4.6 Compression strength test

To determine the effect that mix alterations has on strength gain, the compression strength of each respective mix was determined at various ages in accordance with SANS 5863:2006 (SANS, 2006c). Care was taken to ensure that all extrinsic factors that could affect the measured compression strength was kept constant such as the direction of loading with respect to casting direction, the rate of applied load and specimen size. All prepared samples were stored for 24 hours in a climate control room after which they were demoulded and placed in a temperature-controlled water bath, at 23±1 ℃, for further curing until testing. The compression strength of 100x100x100 mm cubes were measured at a concrete age of 1, 3 and 7 days. The average compression strength of three cubes were used to obtain a single value. Compression tests were performed, using a Contest Compression machine, by loading the cubes perpendicular to the casting direction at a rate of 180 kN/min until failure (Figure 3.9). The compression stress was then calculated using Equation 3.9.

$$\sigma_{cc} = \frac{P}{A} \qquad 3.9$$

Where

$\sigma_{cc} = specimen\ compressive\ strength\ [MPa]$

$P = measured\ force\ at\ failure\ [kN]$

$A = loaded\ surface\ area\ (100x100\ mm)\ [mm^2]$

*Figure 3.9 Contest cube compression machine*

# Chapter 4: Experimental results

This chapter provides a detailed discussion of the results obtained. These results quantify the influence of calcium sulphate to plasticiser/superplasticiser interaction on the overall performance of concrete.

## 4.1 Solubility tests

Table 4.1 shows a summarisation of the experimental results obtained for solubility tests, presenting the influence of the presence and type of plasticiser/superplasticiser used, on the solubility of calcium sulphate.

*Table 4.1 Influence of plasticiser/superplasticiser on the solubility of calcium sulphate*

| **Solution** | **Solubility, $CaSO_4$ g / 100g water** | | | | | |
|---|---|---|---|---|---|---|
| | **Dihydrate** | | | **Hemihydrate** | | |
| | **Average** | **Standard deviation** | **COV** | **Average** | **Standard deviation** | **COV** |
| **Water** | 0,360 | 0,014 | 3,76% | 0,440 | 0,056 | 12,62% |
| **Water containing PCE** | 0,537 | 0,016 | 3,06% | 0,830 | 0,037 | 4,43% |
| **Water containing SNF** | 0,604 | 0,017 | 2,86% | 0,679 | 0,068 | 10,06% |
| **Water containing LS** | 0,466 | 0,032 | 6,82% | 0,731 | 0,097 | 13,30% |

Figure 4.1 presents a visual representation of the influence of plasticiser/superplasticiser on the respective solubility of dihydrate and hemihydrate. All values were normalised w.r.t to the solubility of dihydrate in a pure water solution.

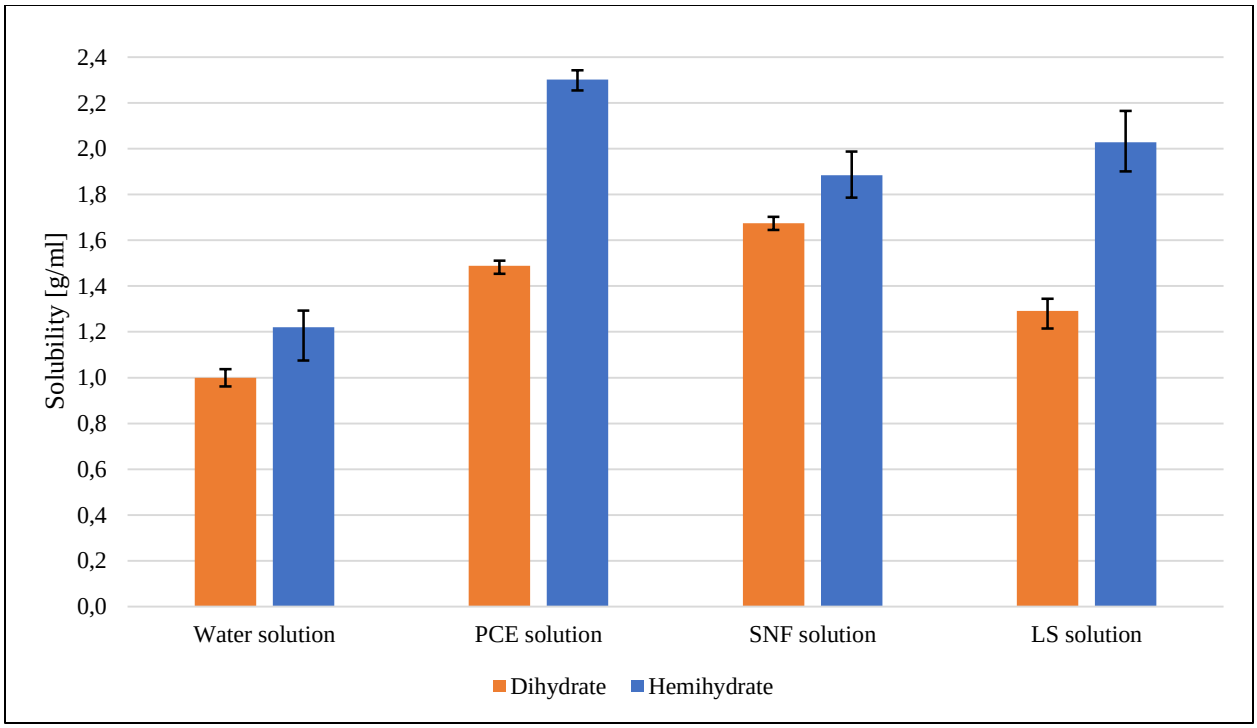


*Figure 4.1 Influence of plasticiser/superplasticiser on the solubility of calcium sulphate (normalised w.r.t dihydrate solubility in pure water)*

From Figure 4.1 it can be seen that hemihydrate has a higher solubility than dihydrate in pure water. When a mixture of water and plasticiser/superplasticiser is used as a solvent the solubility of hemihydrate remained higher than that of dihydrate irrespective of the type of plasticiser/superplasticiser used. Furthermore, the presence of plasticiser/superplasticiser in solution causes an increase in the solubility of calcium sulphate, irrespective of the type of calcium sulphate. It is observed that the solubility of hemihydrate, in general, increased significantly more in the presence of plasticiser/superplasticiser compared to that of dihydrate. However, the type of plasticiser/superplasticiser also showed an influence on solubility. PCE type superplasticiser caused the most significant increase in calcium sulphate solubility, the solubility of hemihydrate being far higher than that of dihydrate. SNF type superplasticiser showed a similar influence on the solubility of calcium sulphate, however the influence of the type of calcium sulphate not being as noteworthy. Conversely, LS type superplasticiser caused a significant increase in the solubility of hemihydrate while only causing a slight increase in the solubility of dihydrate. The solubility of calcium sulphate is therefore dependent on both the type of calcium sulphate and type of plasticiser/superplasticiser present in cement.

## 4.2 Hydration temperature development tests

The temperature during hydration was monitored to determine the influence of the type of calcium sulphate and relation between calcium sulphate and plasticiser/superplasticiser on hydration. The result was a quantitative graph that shows how the length of the “dormant period” changes due to the type of calcium sulphate present in concrete. The hydration temperature curve characteristics of interest are as illustrated in Figure 4.2.

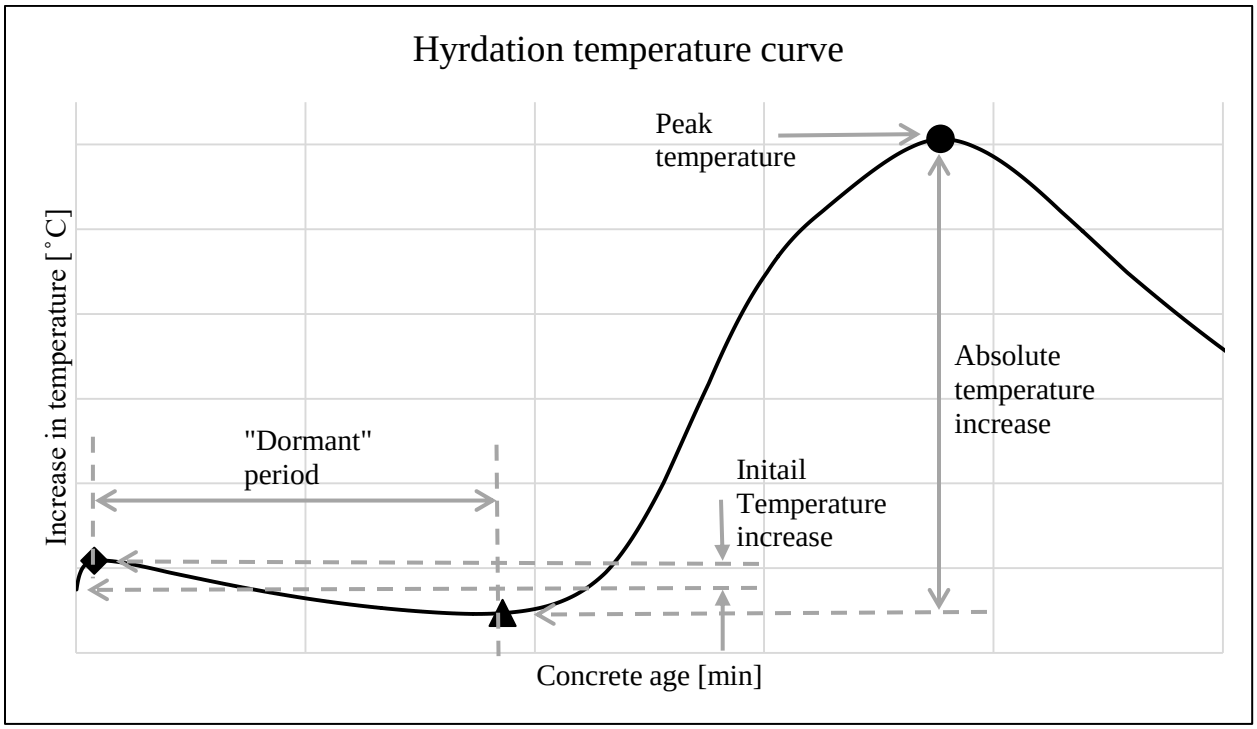


*Figure 4.2 Hydration temperature measurement*

Four characteristic features were observed in the temperature hydration curves i.e. the initial temperature increase, “dormant period”, peak temperature and absolute temperature increase, a distinctive trend being observed for all four features. The initial temperature increase was measured as the increase in temperature from test initiation to the point of first decrease in temperature. This first decrease in temperature indicates the start of the “dormant period”. The “dormant period” continues until a second increase in temperature is measured. All “dormant periods”, presented in Table 4.2 are rounded to the nearest 5 minutes. The peak temperature is the highest temperature recorded during hydration. The absolute temperature increase is measured as the temperature difference between the lowest temperature recorded during hydration and the peak temperature.

Table 4.2 presents a summary of the four observed characteristic features for each mix. Each temperature hydration curve represents the average hydration temperature measured on three samples. The largest standard deviation and coefficient of variance (COV) in hydration temperature between the three samples are presented in Table 4.2.

*Table 4.2 Characteristic features obtained from hydration temperature curve*

| | Initial temp increase [℃] | Dormant period [min] | Absolute temp increase [℃] | Peak Temp [℃] | Largest value over duration of temperature curve | |
|---|---|---|---|---|---|---|
| | | | | | Standard deviation [℃] | COV |
| **Ref** | 0,5 | 50 | 11,9 | 36,8 | 0,727 | 1,78% |
| **4DH** | 0,1 | 80 | 10,2 | 34,3 | 0,447 | 1,04% |
| **4HH** | 0,4 | 50 | 9,6 | 34,1 | 0,263 | 0,71% |
| **2PCE** | 0,2 | 175 | 12,7 | 37,1 | 0,662 | 1,87% |
| **2PCE4DH** | 0,2 | 175 | 11,0 | 35,7 | 0,414 | 0,97% |
| **2PCE4HH** | 0,9 | 205 | 9,1 | 33,8 | 0,166 | 0,51% |
| **2SNF** | 0,4 | 900 | 11,2 | 35,1 | 0,567 | 1,47% |
| **2SNF4DH** | 0,6 | 1040 | 11,4 | 35,6 | 0,205 | 0,69% |
| **2SNF4HH** | 0,7 | 630 | 10,3 | 34,7 | 0,376 | 0,91% |
| **2LS** | 0,9 | 355 | 11,2 | 35,9 | 0,662 | 1,87% |
| **2LS4DH** | 0,6 | 325 | 10,4 | 35,1 | 0,344 | 0,81% |
| **2LS4HH** | 1,3 | 285 | 10,0 | 34,7 | 0,807 | 2,00% |

Figure 4.4 presents the high degree of repeatability and accuracy achieved, as very similar hydration temperature curves are recorded for samples that have the same mix design.

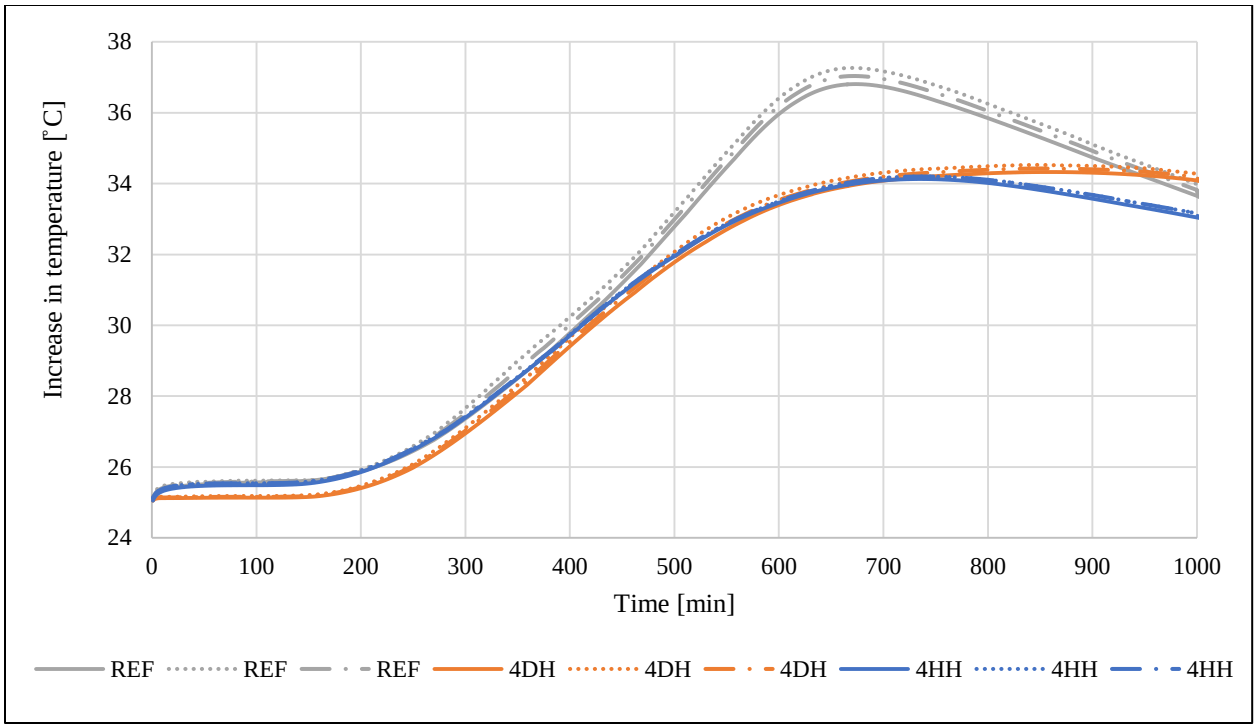


*Figure 4.3 Three temperature hydration curves per mix design; each sample (that has the same mix design) presenting similar recorded temperatures.*

As presented in Figure 4.4 to Figure 4.7 and Table 4.2 the presence of hemihydrate is observed to cause a slightly higher initial increase in temperature when the temperature curve of mixes substituted with dihydrate (-4DH) is compared with mixes substituted with hemihydrate (-4HH). This could be as a result of hemihydrate rehydration (Singh and Middendorf, 2007). The rehydration of hemihydrate is a strong exothermic reaction, which results in an increase in measured initial hydration temperature. This would also suggest the mix REF contains a greater proportion of hemihydrate than dihydrate, due to its initial increase in temperature being similar to that of mix 4HH. Thereafter the dissolution of tricalcium aluminate and precipitation of ettringite occurs simultaneously, allowing for a dormant period (Pourchet *et al.*, 2009).

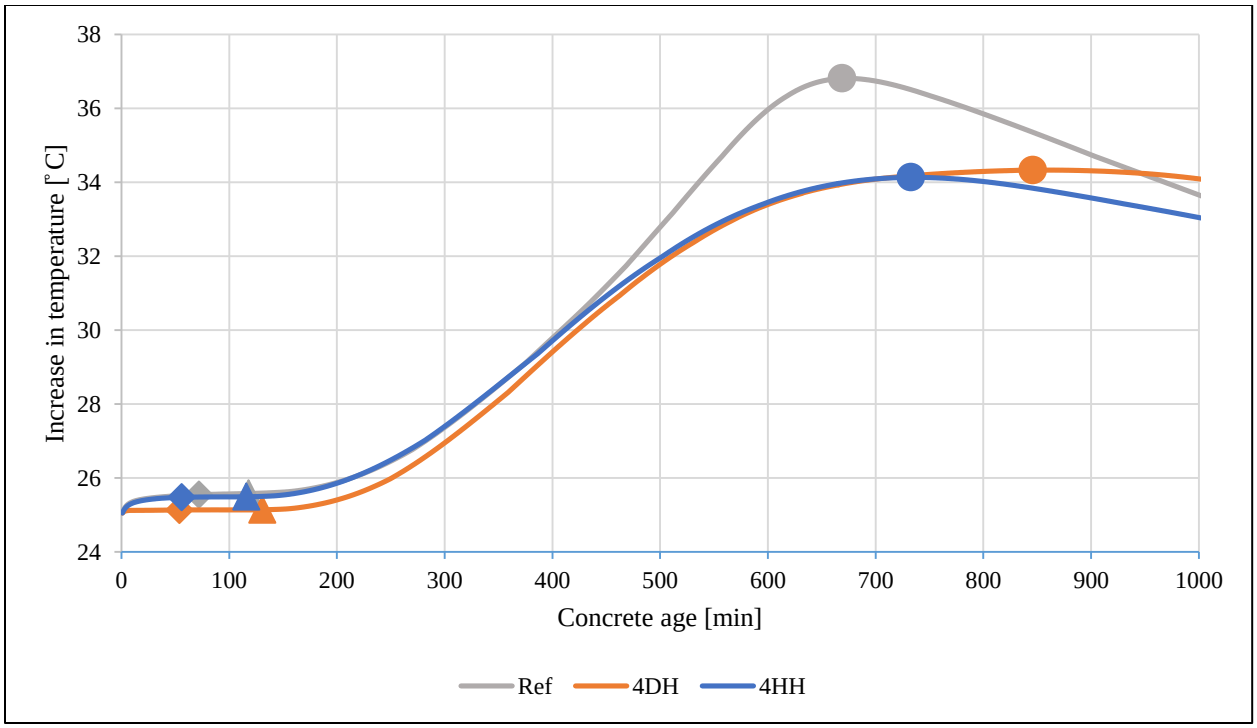


*Figure 4.4 Influence of calcium sulphate on hydration temperature build up*

Furthermore, it is observed that this increase in initial temperature is proportional to the influence of each plasticiser/superplasticiser on the solubility of calcium sulphate as discussed in Section 4.1. Mixes containing hemihydrate, in conjunction with PCE and LS, showed a significant increase in initial hydration temperature compared to mixes containing SNF type superplasticiser as seen in Figure 4.6. This concurs with the higher increase in hemihydrate solubility caused by PCE and LS, compared to that of SNF type superplasticiser. The SNF type superplasticiser, however, showed less sensitivity to the type of calcium sulphate present with regard to the initial temperature increase. This would indicate that SNF type superplasticiser has a similar influence on the solubility of both dihydrate and hemihydrate, as is confirmed by Table 4.1 in Section 4.1. The initial fresh state properties of concrete mixes containing SNF type superplasticiser should therefore show less sensitivity to the type of calcium sulphate present in cement.

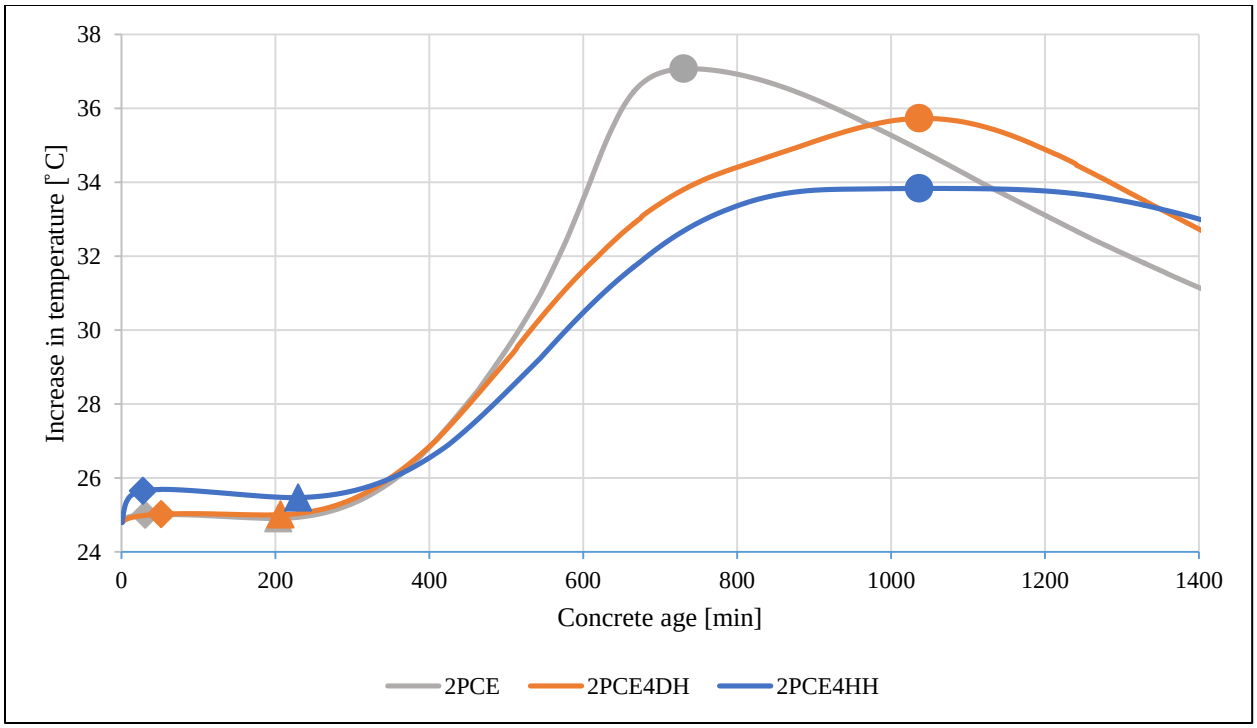


*Figure 4.5 Influence of calcium sulphate – PCE type superplasticiser relation on hydration temperature build up*

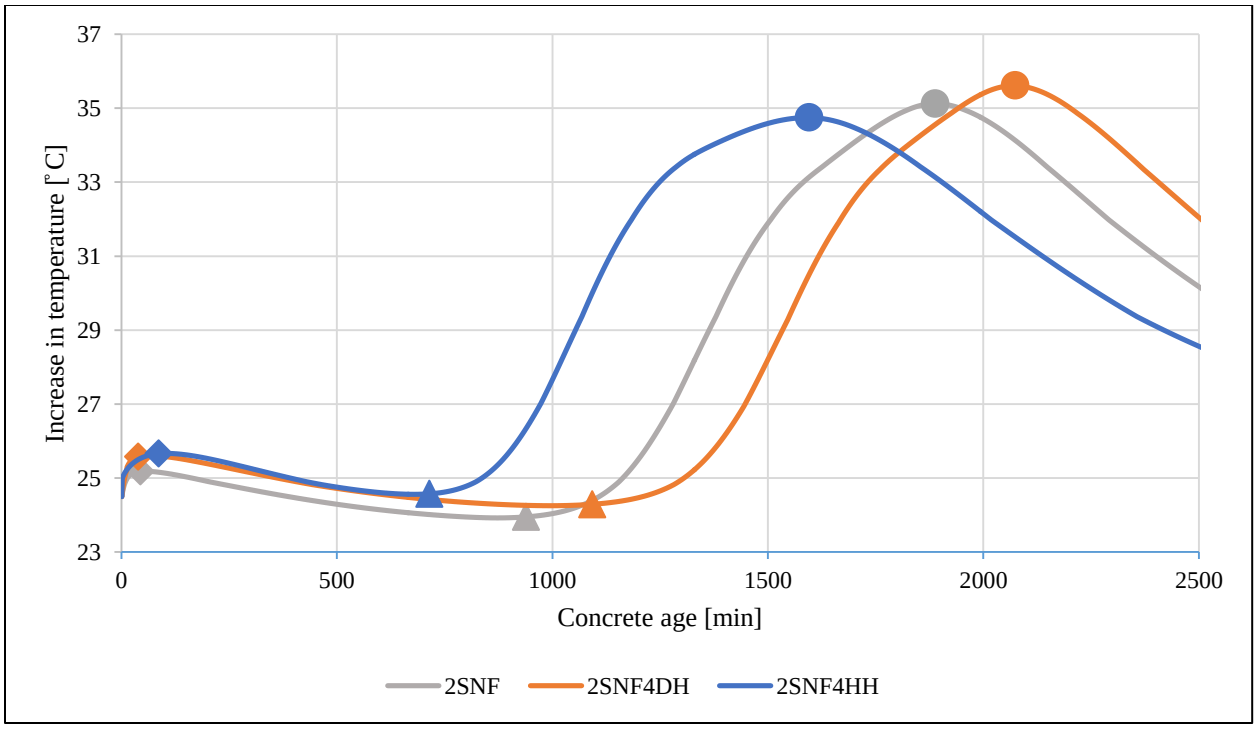


*Figure 4.6 Influence of calcium sulphate – SNF type superplasticiser relation on hydration temperature build up*

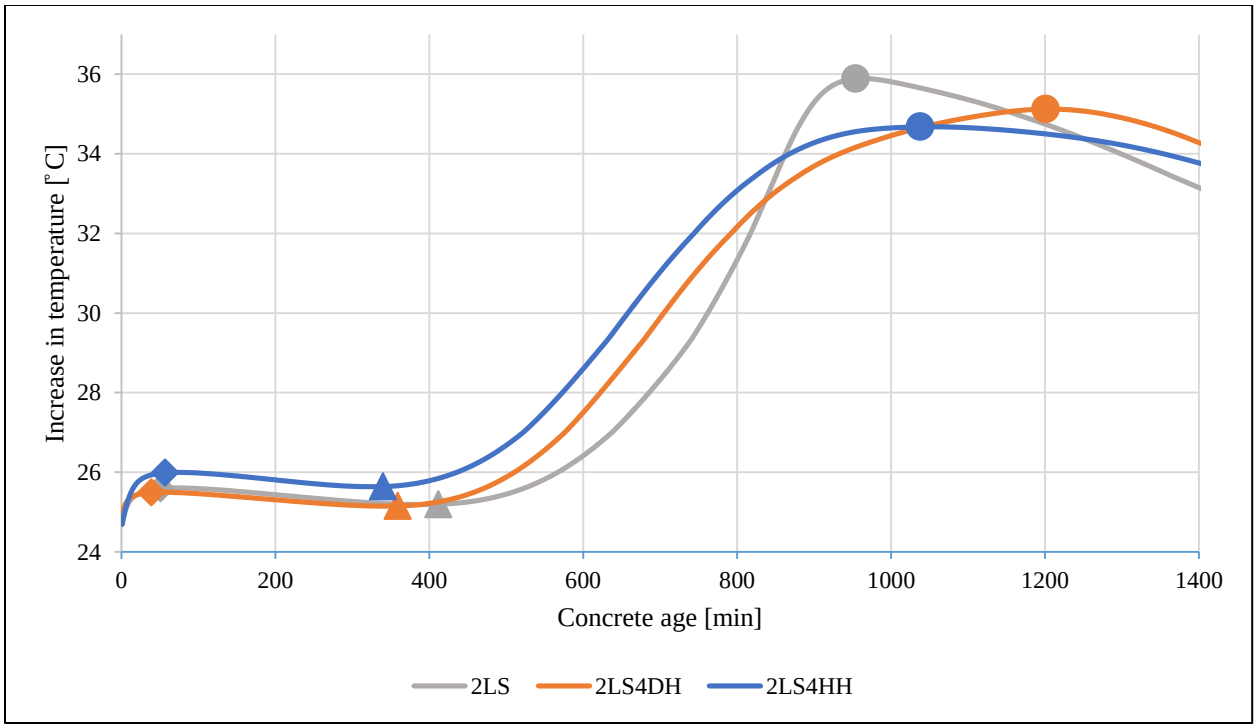


*Figure 4.7 Influence of calcium sulphate - LS type plasticiser on hydration temperature build up*

It is observed that the type of calcium sulphate influences the length of dormant period. Generally, it is noticed that the "dormant period" of mixes containing binder that was partially substituted with hemihydrate is shorter compared to mixes substituted with dihydrate. Mixes containing SNF type superplasticiser showed the highest reduction in dormant period i.e. the time that workability is maintained, in the presence of hemihydrate. The decreased length of "dormant period" of concrete containing SNF type superplasticiser in conjunction with a cement containing high quantities of hemihydrate could present a compatibility issue seeing that SNF type superplasticiser is often used to produce ready mix concrete that has to be transported to sight.

Both dihydrate and hemihydrate showed to cause a reduction in the length of dormant period of mixes containing LS type plasticiser, the influence of the latter being more significant. This reduction in length of dormant period is as a result of the respective solubility (in conjunction with rate of dissolution) of dihydrate and hemihydrate. The higher the solubility of the calcium sulphate, present in cement, the more sulphate ions are freely available within the concrete solution. The rate at which sulphate ions are available within the mix solution modifies the rate of hydration as the rate of ettringite growth is proportionate to the availability of sulphate ions i.e. solubility of calcium sulphate. According to Bensted, 1982 if the availability of dissolved sulphate increases, a

greater degree of hydration will occur at the same concrete age, within the first few hours, due to the growth rate of ettringite increasing. The opposite was found to be true for mixes containing PCE type superplasticiser. Hemihydrate caused an increase in length of dormant period of mixes containing PCE type superplasticiser.

Furthermore, it is observed that the decrease in length of dormant period, caused by the presence of hemihydrate, is dependent on the type of plasticiser/superplasticiser used in mix design. However, in this study no correlation is observed between the magnitude with which the dormant period is shortened and the influence of each respective of plasticiser/superplasticiser on the solubility of calcium sulphate.

Finally, it can be seen that mixes that contain higher dosages of calcium sulphate, introduced through substitution of binder with either dihydrate or hemihydrate, present a lower final hydration temperature. This is due to the addition of calcium sulphate retarding the hydration of the aluminate phase. It is assumed that the time of aluminate phase hydration is superimposed to the time of peak temperature, brought about by the hydration of the silicate phase, in mixes not altered with the addition of calcium sulphate. In calcium sulphate deprived cementitious systems the hydration of the aluminate phase may occur before the hydration of the silicate phase. The opposite is also true for cementitious systems. As the quantity of calcium sulphate is increased the hydration of $C_3A$ i.e. reaction with water, is delayed, causing a secondary peak in hydration temperature that occurs after the first hydration temperature peak caused by the hydration of silicate phase. This causes a smaller, broader second peak to be observed during hydration due to $C_3A$ hydration (Zunino and Scrivener, 2019). However, during the recording of hydration temperature no secondary peak was observed during any of the tests. It is presumed that this due to the test performed not being a fully adiabatic process and the temperature peak caused by aluminate hydration becoming smaller and broader as it shifts to a later time during hydration (Zunino and Scrivener, 2019).

## 4.3 Fresh state properties: ICAR Rheometer, slump and Vicat tests

The fresh state properties of mixes containing various dosages of calcium sulphate, with different chemical nature, in conjunction with variable dosages of different types of plasticiser/superplasticiser are presented in Table 4.3.

*Table 4.3 Influence of calcium sulphate – plasticiser/superplasticiser relation on fresh state properties of concrete*

| Mix | Averaged Slump or Slump flow (if >210) [mm] | Static Yield Stress (SYS) [Pa] | Dynamic Yield Stress (DYS) [Pa] | Thixotropy Potential [Pa] | Plastic Viscosity [Pa.s] | Athix [Pa/min] | Averaged Initial Setting time [min] |
|---|---|---|---|---|---|---|---|
| **REF** | 200 | 815 | 571 | 244 | 22,2 | 12,0 | 125 |
| **2DH** | 180 | 785 | 565 | 221 | 30,1 | 8,8 | 150 |
| **4DH** | 170 | 1026 | 685 | 341 | 31,4 | 6,8 | 130 |
| **2HH** | 170 | 819 | 614 | 205 | 28,4 | 9,9 | 145 |
| **4HH** | 150 | 1036 | 691 | 345 | 43,4 | 23,1 | 105 |
| **PCE** | 430 | 461 | 343 | 118 | 21,4 | 12,3 | 165 |
| **2PCE** | 600 | 249 | 178 | 71 | 28,6 | 5,4 | 185 |
| **2PCE2DH** | 700 | 215 | 128 | 87 | 35,2 | 9,3 | 300 |
| **2PCE2HH** | 580 | 283 | 165 | 118 | 43,0 | 10,0 | 295 |
| **2PCE4DH** | 630 | 225 | 162 | 63 | 33,5 | 4,4 | 255 |
| **2PCE4HH** | 465 | 348 | 238 | 110 | 37,9 | 5,2 | 180 |
| **SNF** | 395 | 723 | 526 | 197 | 20,9 | 9,3 | 265 |
| **2SNF** | 505 | 312 | 233 | 79 | 18,4 | 7,9 | 300 |
| **2SNF2DH** | 635 | 220 | 141 | 79 | 23,3 | 3,7 | >390 |
| **2SNF2HH** | 555 | 229 | 166 | 63 | 24,8 | 12,9 | >390 |
| **2SNF4DH** | 555 | 314 | 196 | 118 | 21,4 | 8,8 | >390 |
| **2SNF4HH** | 575 | 456 | 338 | 118 | 28,3 | 26,0 | >390 |
| **LS** | 325 | 756 | 583 | 173 | 35,0 | 8,7 | 165 |
| **2LS** | 390 | 504 | 378 | 126 | 33,8 | 8,8 | 165 |
| **2LS2DH** | 385 | 479 | 377 | 102 | 22,4 | 7,6 | 265 |
| **2LS2HH** | 380 | 645 | 479 | 166 | 37,9 | N/A (false set) | 170 |
| **2LS4DH** | 360 | 569 | 419 | 150 | 33,3 | 11,3 | 270 |
| **2LS4HH** | 330 | 867 | 568 | 300 | 39,5 | N/A (false set) | 170 |

### 4.3.1 Calcium sulphate

From the results obtained it is evident that the type of calcium sulphate influences the initial fresh state properties of concrete, as presented in Figure 4.8.

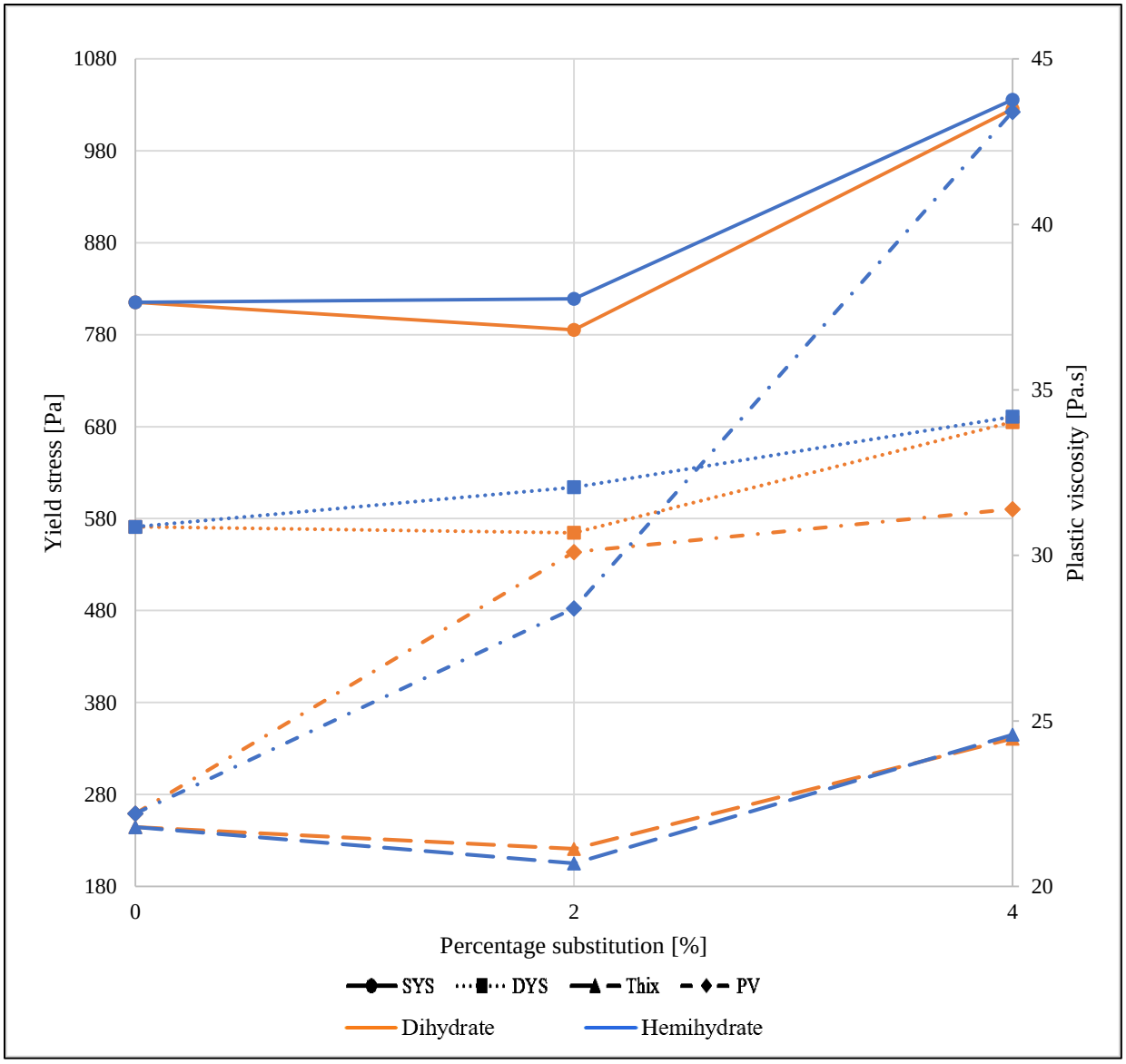


*Figure 4.8 Influence of type of calcium sulphate on initial fresh state properties*

The increase in calcium sulphate in cement showed an increase in the water demand of concrete. This is predicted to be a result of the higher fineness of both dihydrate and hemihydrate, compared to the cement fineness as presented by the Blaine fineness in Table 3.4. This was evident in the decrease in slump measured, the presence of hemihydrate causing a larger decrease slump than dihydrate. This is supported by the increase in SYS of mixes 2HH and 4HH being greater than that of mixes 2DH and 4DH. Mixes containing hemihydrate showed a higher increase in water demand due to the rehydration of hemihydrate before dissolution. Furthermore, the results show that the influence of the nature of the calcium sulphate, being either dihydrate or hemihydrate, on the water

demand of concrete does not change significantly with dosage. At 2% substitution of cement with calcium sulphate a decrease in initial thixotropy was measured, however thixotropy increases at a higher dosage as measured in mixes 4DH and 4HH. An increase in plastic viscosity is also measured with the substitution of calcium sulphate, viscosity increasing significantly at higher dosages of hemihydrate compared to that of dihydrate.

To evaluate the influence of either dihydrate or hemihydrate on the rate or structuration i.e. the rate at which concrete stiffens, five successive Stress Growth tests were conducted with incremental periods of rest allowed between each test. The results are as depicted in Figure 4.9.

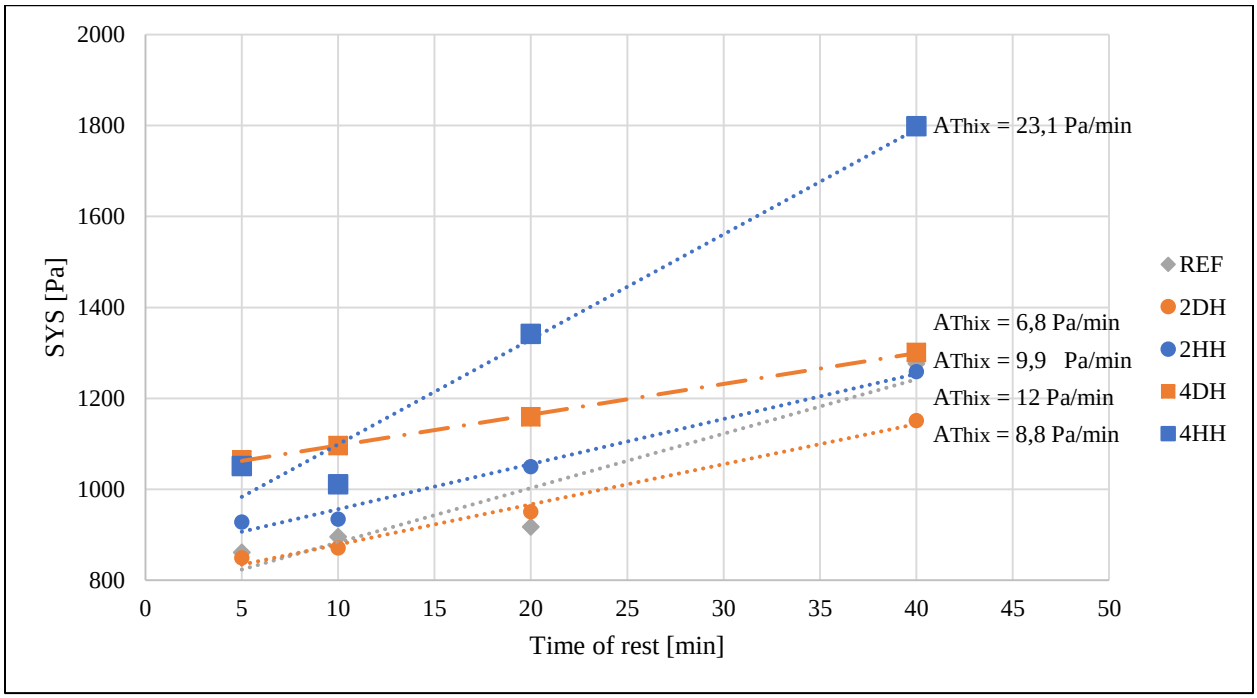


*Figure 4.9 Influence of type of calcium sulphate on the rate of structuration of concrete*

The results from Figure 4.9 are consolidated into Figure 4.10. From Figure 4.10 it can be seen that the nature of the calcium sulphate present in cement has a noteworthy influence on the period that fluidity/workability is maintained, particularly at higher dosages.

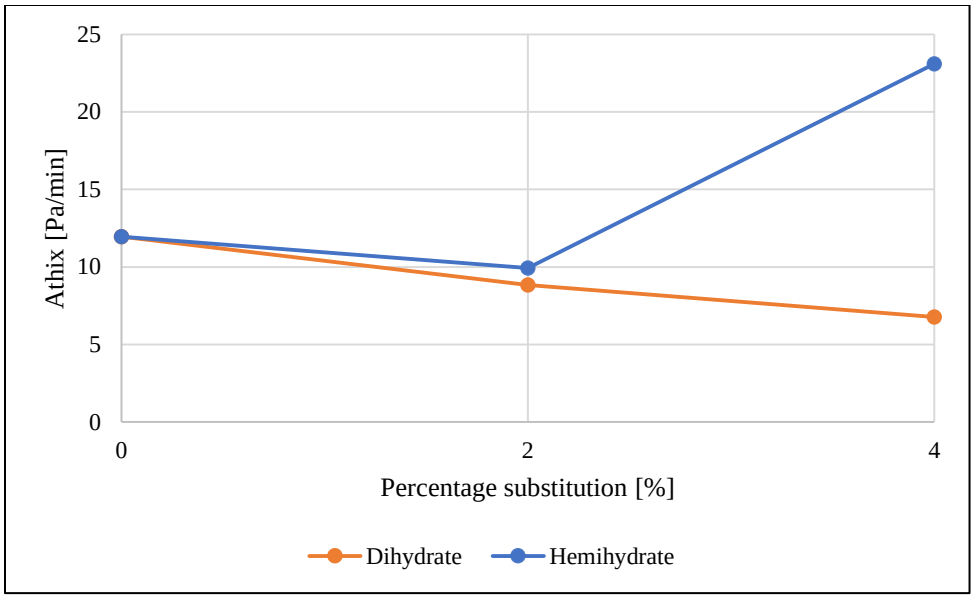


*Figure 4.10 Influence of the type of calcium sulphate on the rate of structuration.*

At 2% substitution of concrete with calcium sulphate both dihydrate and hemihydrate showed a decrease in the rate of structuration. It is presumed that this decrease in the rate of structuration is caused by the method used to increase the calcium sulphate content. In order to keep the binder content constant some cement (containing both clinker and calcium sulphate) were removed and replaced with only calcium sulphate. This reduced the quasi contact points at which CSH bridges can form during the early phases of hydration, however, it should be noted that this decrease in $A_{Thix}$ is more prominent with dihydrate. At 4% substitution, it is seen that $A_{Thix}$ decreases further in mix 4DH. On the other hand, mix 4HH showed a significant increase in $A_{Thix}$. It can therefore be concluded that the presence of hemihydrate in cement increases the rate of structuration i.e. the rate at which concrete stiffens, this being more prominent the higher the volume of hemihydrate present. This could once again be explained by the higher solubility of hemihydrate, compared to that of dihydrate. The higher solubility of hemihydrates results in sulphates being more freely available to react with tricalcium aluminates, accelerating the formation of ettringite, which results a matrix of entangled ettringite crystals forming that increases the stiffness of concrete in the fresh state. The same trend was noticed in the initial setting time. The initial setting time of mixes 2DH and 2HH increased, the increase being larger for dihydrate. A further increase in initial setting time was noticed in mix 4DH, while mix 4HH showed a decrease in initial setting time of 20 min w.r.t mix REF. Similar results were obtained by García-Maté *et al.*, (2015) when investigating the influence of the type of calcium sulphate on the hydration of eco-cement. It was found that the use

of hemihydrate caused a reduction in setting time when compared to mixes containing dihydrate. This can be as a result of the faster dissolution of hemihydrate resulting in the earlier and accelerated formation of ettringite (Bensted, 1982).

It is evident that the temperature during milling of clinker and dihydrate (gypsum), to form cement, should be regulated to control the quantity of dihydrate that is converted to hemihydrate and anhydrite. From the results shown it is evident that the presence of hemihydrate increases the water consumption of cement. The presence of hemihydrate in cement has a negligible influence on the SYS and thixotropy of concrete but causes a significant increase in concrete PV and rate of structuration. Hemihydrate causes accelerated stiffening of concrete, therefore reducing the time available for casting and finishing of concrete. The influence of hemihydrate in cement, on some practical aspects, can be seen in Figure 4.11. It should be noted that Figure 4.11 only indicates the characteristic performance of each mix with respect to the other mixes. From the results in Figure 4.11 it can be seen that the presence of hemihydrate instead of dihydrate, as source of calcium sulphate in cement, lowers formwork pressure as well as the risk of segregation of concrete. However, the presence of hemihydrate in cement also results in an increase in pumping pressure. The combined increase in SYS and PV of concrete with high quantities of hemihydrate also increases the amount of vibration required to remove entrapped air, therefore, increasing the risk of bugholes on the concrete surface.

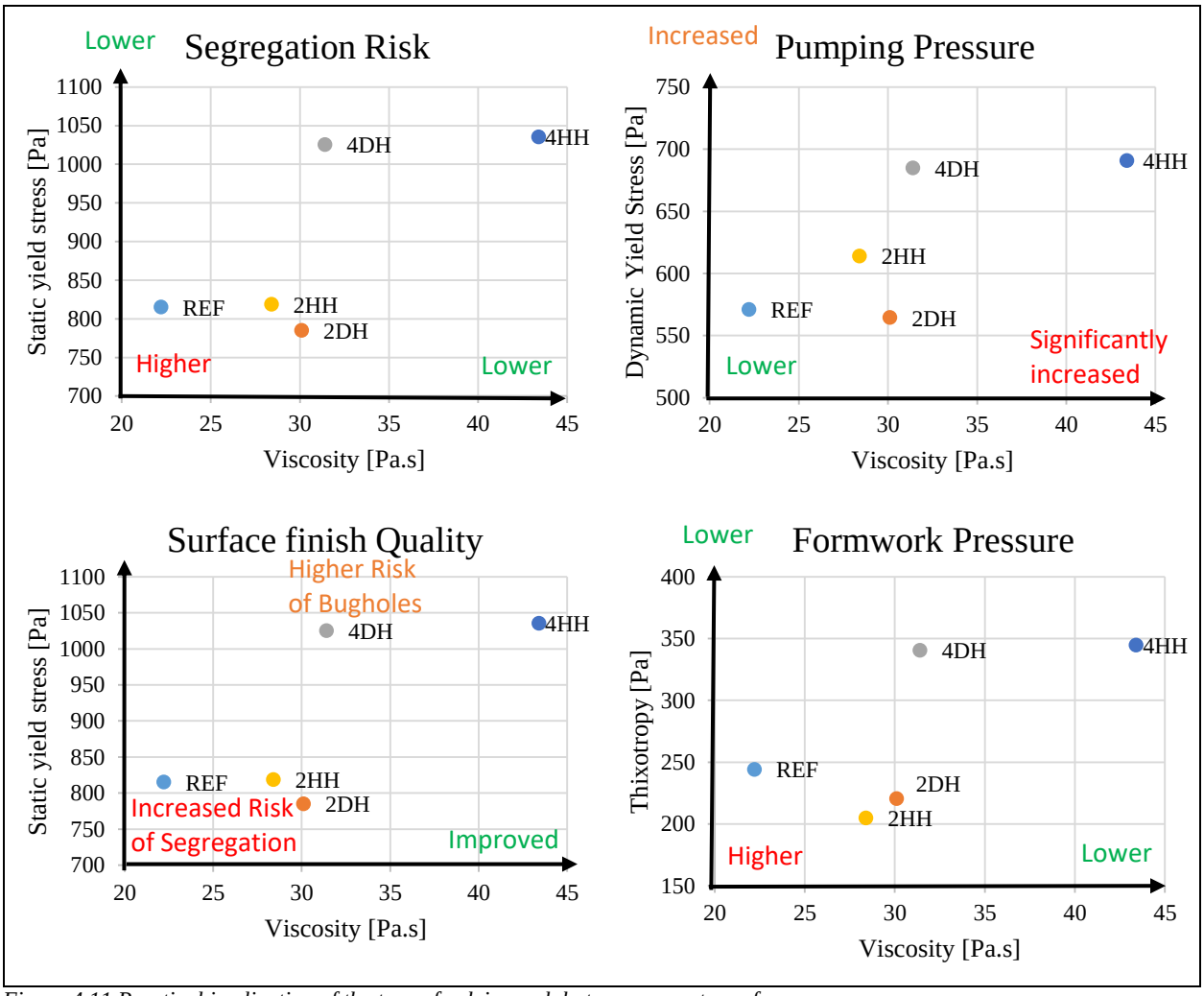


*Figure 4.11 Practical implication of the type of calcium sulphate on concrete performance*

## 4.3.2 Plasticiser/ superplasticiser

Figure 4.12 presents the influence of all plasticisers/superplasticisers used on the rheological properties of concrete.

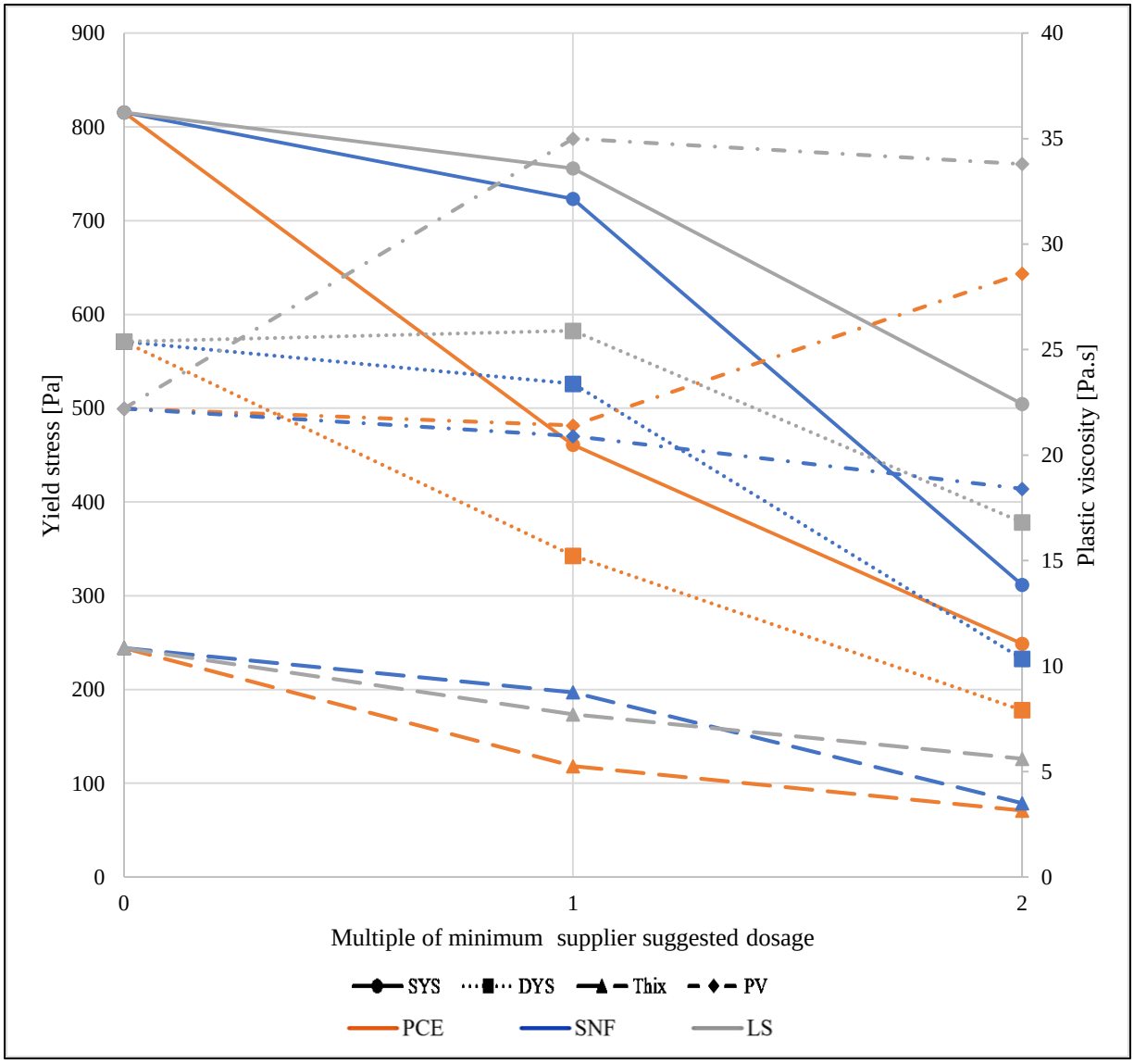


*Figure 4.12 Influence of superplasticiser on initial fresh state properties*

All plasticiser/superplasticisers caused an increase in slump flow with a corresponding decrease in SYS. This is due to plasticiser/superplasticiser decreasing the water consumption of the mix through the working mechanisms discussed in Section 2.5.1. A decrease in thixotropy was also observed through the addition of plasticiser/superplasticiser. Both these characteristics of plasticisers/superplasticiser increase with an increase in dosage. It is interesting to note that the use of PCE and LS type plasticiser/superplasticiser caused an increase in plastic viscosity, the viscosity increases with an increase in PCE dosage whereas the increase in LS dosages only showed a slight decrease in plastic viscosity (PV) at higher dosages but still being higher than the PV measured in mix REF. Apparent viscosity is defined as a measurement of resistance to flow

caused by the internal particle friction and particle bonds. At the early age of cementitious materials, only flocculation contributes to the internal structure, however seeing that plasticisers and superplasticiser delays flocculation one would expect a decrease in plastic viscosity (Kruger, Zeranka and Zijl, 2019). However, this behaviour was only observed with the SNF type superplasticiser used. The results obtained would therefore suggest that PCE and LS type plasticiser/superplasticiser increases concrete fluidity without decreasing mix cohesion (viscosity) at the considered dosages. This could be due to the addition of air detainers to the plasticiser/superplasticiser as is done extensively by manufacturers. This is to detrain, as the name suggests, a significant amount of air within the products and therefore within the concrete mix that would otherwise be introduced through the addition of either plasticisers and/or superplasticisers. The addition of air detainers will prevent the plasticiser/superplasticiser from entraining more than 2 % air in the concrete (Chryso SA, 2007). This addition of air detainer could increase the viscosity of a concrete mix.

All plasticisers/superplasticisers delayed the stiffening of concrete as seen in Figure 4.13, measured as the rate of structuration.

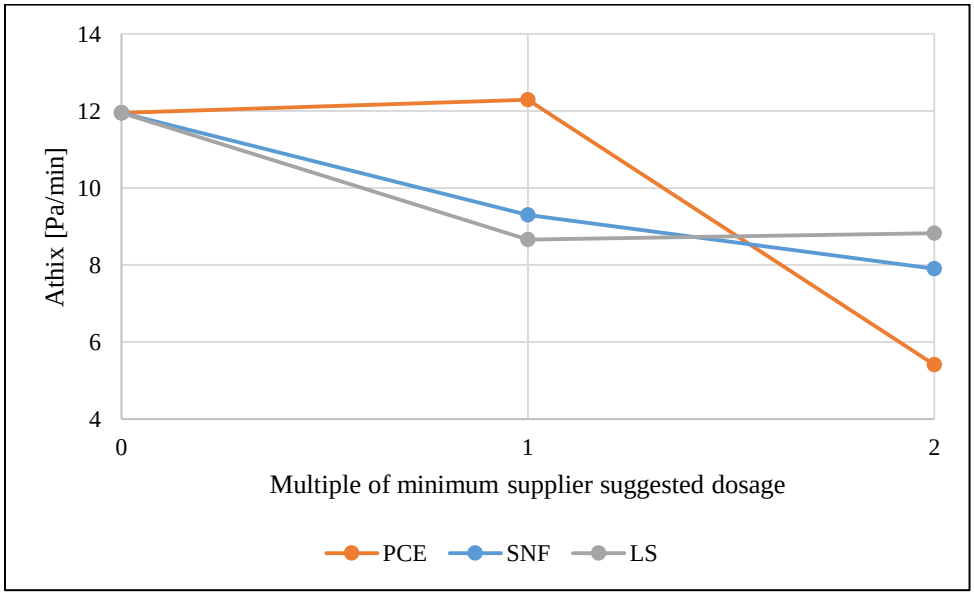


*Figure 4.13 Influence of plasticiser/superplasticiser on the rate of structuration*

This delay in structuration increased with an increase in superplasticiser dosage. LS type plasticiser, however, showed a negligible change in $A_{Thix}$ with an increase in dosage. It is also interesting the note that although the use of LS type plasticiser caused an increase in initial setting time, this increase remained constant when the dosage of LS type plasticiser increased. PCE and SNF type superplasticiser delayed initial setting time, this delay in initial setting time increasing with an increase in dosage.

The influence of the use of plasticiser/superplasticiser in concrete mix design on some practical performance criteria of concrete are presented in Figure 4.14. From Figure 4.14 it is seen that the use of LS type superplasticiser presents the lowest risk of segregation, followed by PCE - and SNF type superplasticiser at the dosages used. This is due to LS type plasticiser causing a decrease in SYS without decreasing PV. However, this also results in increased pumping pressures. SNF – and PCE type superplasticiser therefore being more beneficial when decreased pumping pressures are desired. On the other hand, high thixotropy and PV is desirable when formwork pressures present a problem. LS type plasticiser or PCE type superplasticiser, depending on the desired workability, should therefore be considered when decreased formwork pressure is desired as the use of SNF type superplasticiser can cause significant formwork pressures.

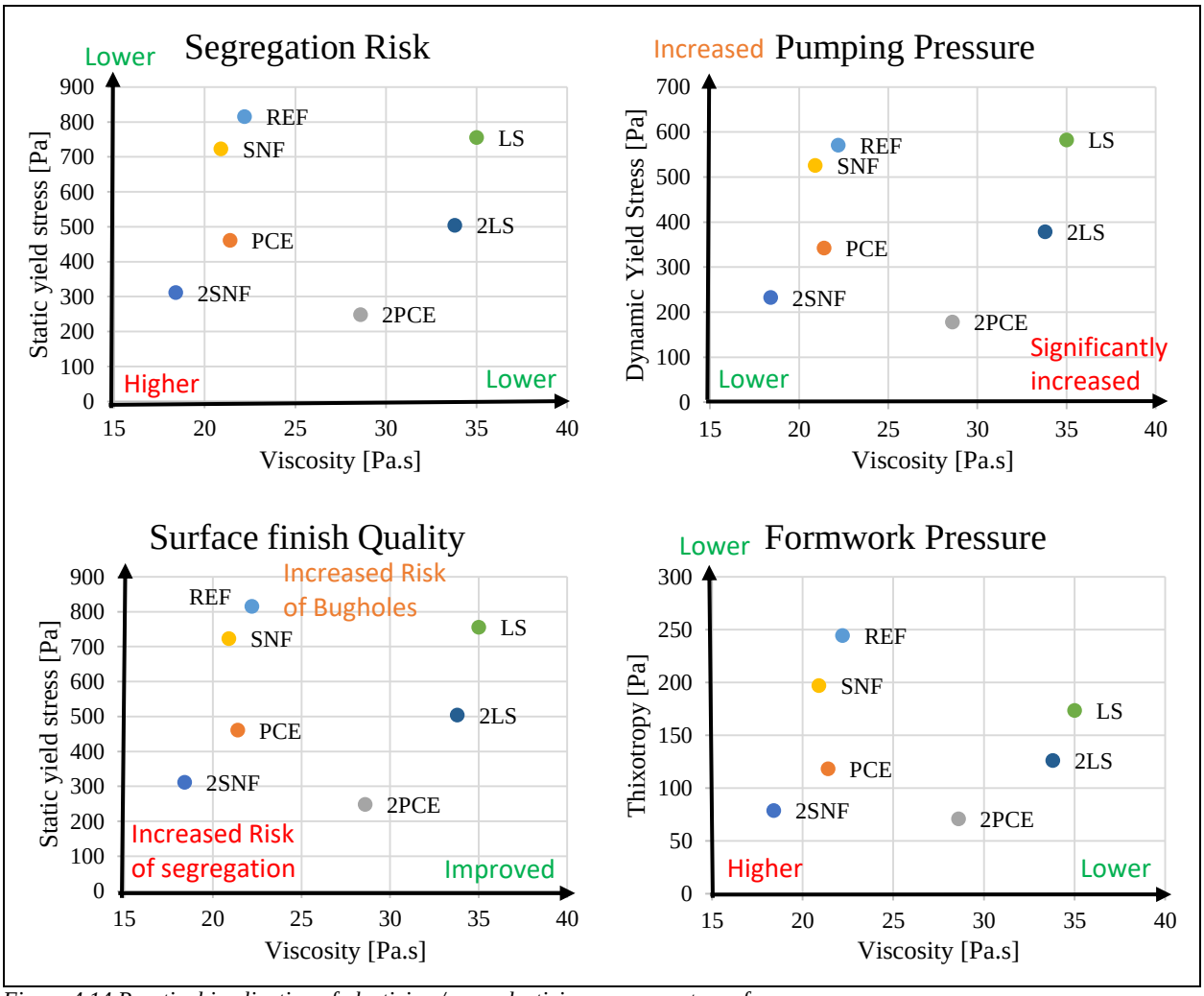


*Figure 4.14 Practical implication of plasticiser/superplasticiser on concrete performance*

### 4.3.3 Calcium sulphate to plasticiser/superplasticiser interaction

The loss of fluidity in cementitious materials are connected to the hydration of tricalcium aluminates in the presence of calcium sulphate to form ettringite. As ettringite starts to precipitate a microstructure of entangled ettringite crystals form that dominates the initial structuration of concrete. This structuration is dependent on the type of calcium sulphate and plasticiser/superplasticiser used in concrete mix design as sulphate ions and plasticiser/superplasticiser compete to react with tricalcium aluminates. Therefore, the fresh state properties of concrete can be controlled if the interaction between the calcium sulphate and plasticiser/superplasticiser are known.

#### 4.3.3.1 PCE type superplasticiser

From the results obtained it was found that the nature of the calcium sulphate present in cement affects the influence of PCE type superplasticiser on the fresh state properties of concrete without significantly influencing hydration, as presented in Figure 4.15 and Figure 4.16.

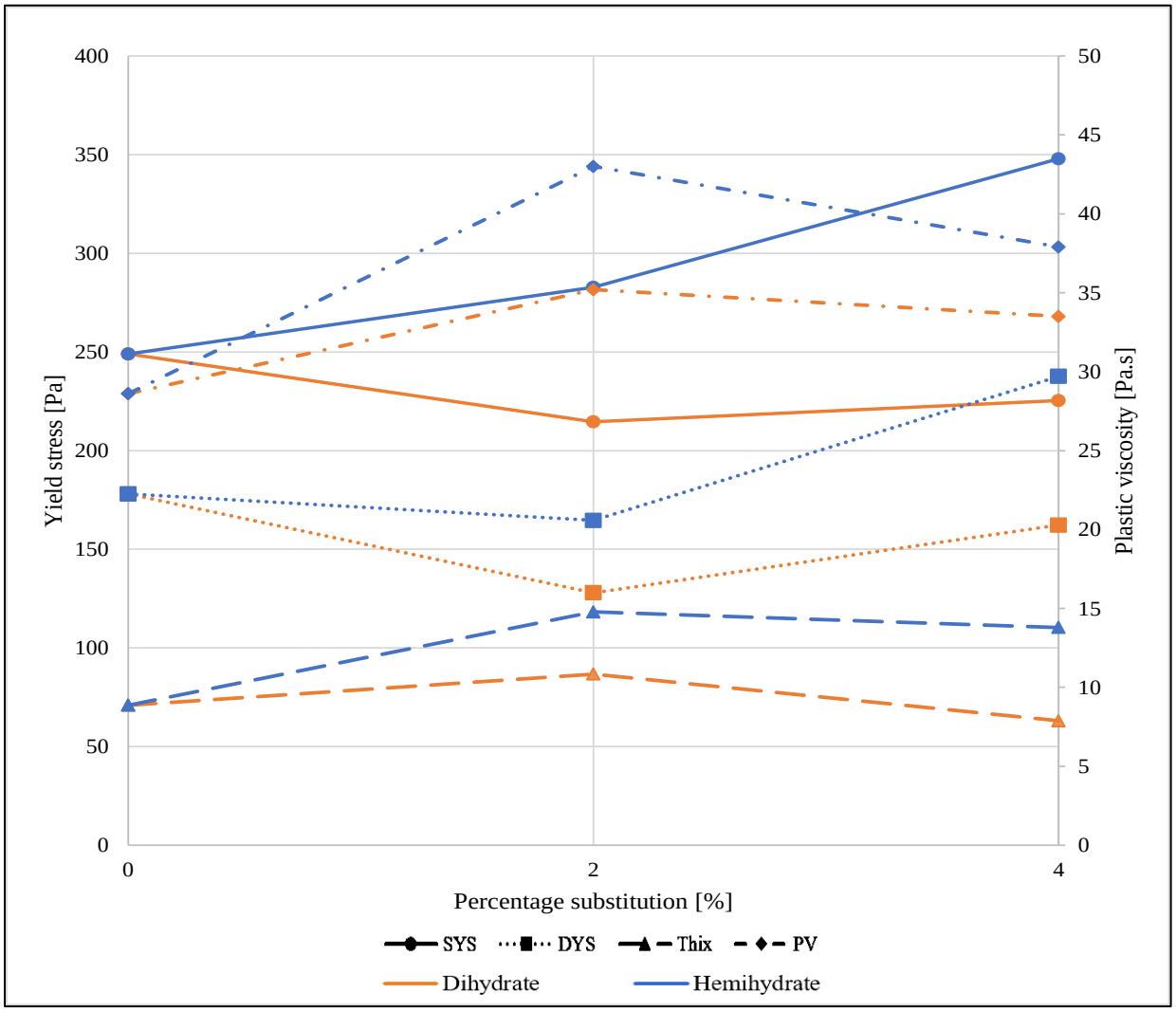


*Figure 4.15 Influence of PCE type superplasticiser – calcium sulphate interaction on initial fresh state properties*

The presence of hemihydrate caused a significant decrease in slump and an increase in initial SYS, this phenomenon increases with an increase in hemihydrate dosage. Dihydrate, on the other hand, caused an increase in slump with a corresponding decrease in initial SYS. This can be explained by considering the influence of PCE type superplasticiser on the solubility of hemihydrate as presented in Section 4.1. PCE type superplasticiser significantly increases the solubility of hemihydrate, however, hemihydrate rehydrates before dissolution, therefore increasing the water

consumption of concrete. Furthermore, the presence of hemihydrate caused an increase in mix thixotropy and plastic viscosity. The type of calcium sulphate has no significant influence on the rate of structuration of concrete that contains PCE type superplasticiser, PCE type superplasticiser being more sensitive to the quantity of calcium sulphate (as seen in Figure 4.16).

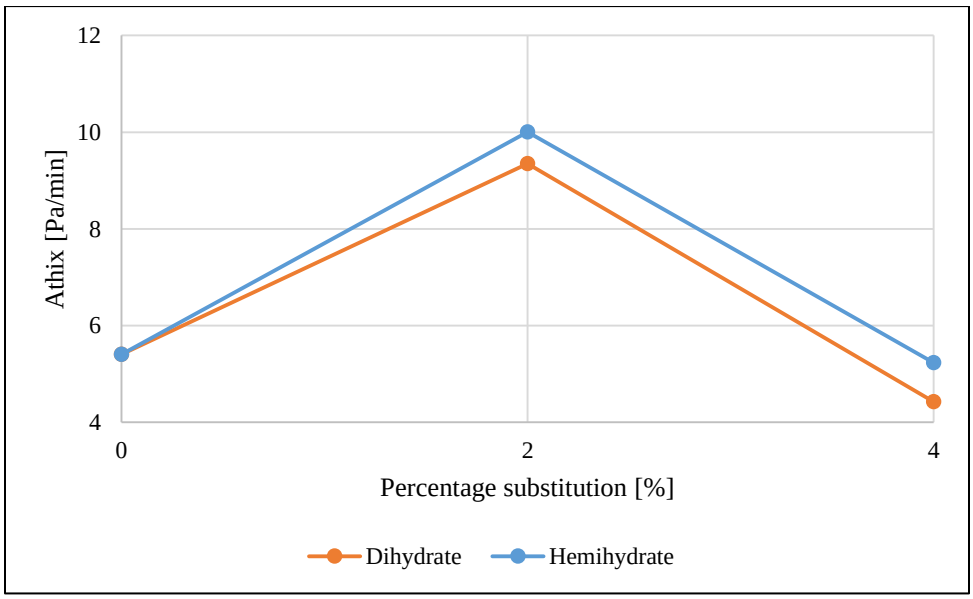


*Figure 4.16 Influence of PCE type superplasticiser – calcium sulphate interaction on the structuration rate of concrete*

The nature of the calcium sulphate showed no significant influence on the structuration rate, irrespective of the dosage, on concrete containing PCE type superplasticiser. This behaviour is unexpected when the influence of PCE type superplasticiser on the solubility of hemihydrate, compared to that of dihydrate, is taken into account. It is expected that concrete mixes containing PCE type superplasticiser and hemihydrate would show accelerated structuration due to PCE type superplasticiser increasing the solubility of hemihydrate significantly, therefore increasing the amount of sulphates available to react with tricalcium aluminates which would accelerate ettringite formation. This could indicate that PCE type superplasticiser delays the hydration of tricalcium aluminates and therefore the formation of ettringite, causing the nature and solubility of calcium sulphate to have negligible effect on the rate of structuration. However, PCE type superplasticiser is affected by the dosage of calcium sulphate, the rate of structuration increasing at 2% substitution whereas no significant change in the rate of structuration is noticed at 4% substitution. Furthermore, no correlation was found between $A_{Thix}$ and the initial setting time. The presence of

hemihydrate caused a reduction in initial setting time, this becoming more significant at higher dosages of hemihydrate.

Hemihydrate therefore significantly reduces the effectiveness of PCE superplasticiser as a liquidizing agent, as was supported by the decrease in slump flow and increase in initial SYS, without influencing the rate at which it loses fluidity thereafter. This could be due to PCE type superplasticiser having an affinity for the intermediate cubic hydration product $C_3A$ formed before the formation of ettringite. It was found that these intermediate $C_3A$ hydration products don't form in the presence in hemihydrate (Pourchet *et al.*, 2009). PCE type superplasticiser will thus influence the initial reaction between tricalcium aluminates and calcium sulphate by reacting with the intermediate $C_3A$ hydration products while sulphate ions are not available within the concrete pore solution. The increased solubility of hemihydrate allows for a reaction between tricalcium aluminates and dissolved sulphate ions to form ettringite, before interaction with PCE type superplasticiser.

The implications of the interaction between calcium sulphate and PCE type superplasticiser on the practical application of concrete is presented in Figure 4.17.Figure 4.17 shows that using hemihydrate as a source of calcium sulphate reduces the risk of segregation of concrete containing PCE type superplasticiser due to an increase in viscosity. However, this results in an increase in pumping pressures. Furthermore, a decrease in formwork pressure and increase surface finish quality occurs when hemihydrate is used as a source of calcium sulphate in concrete containing PCE type superplasticiser.

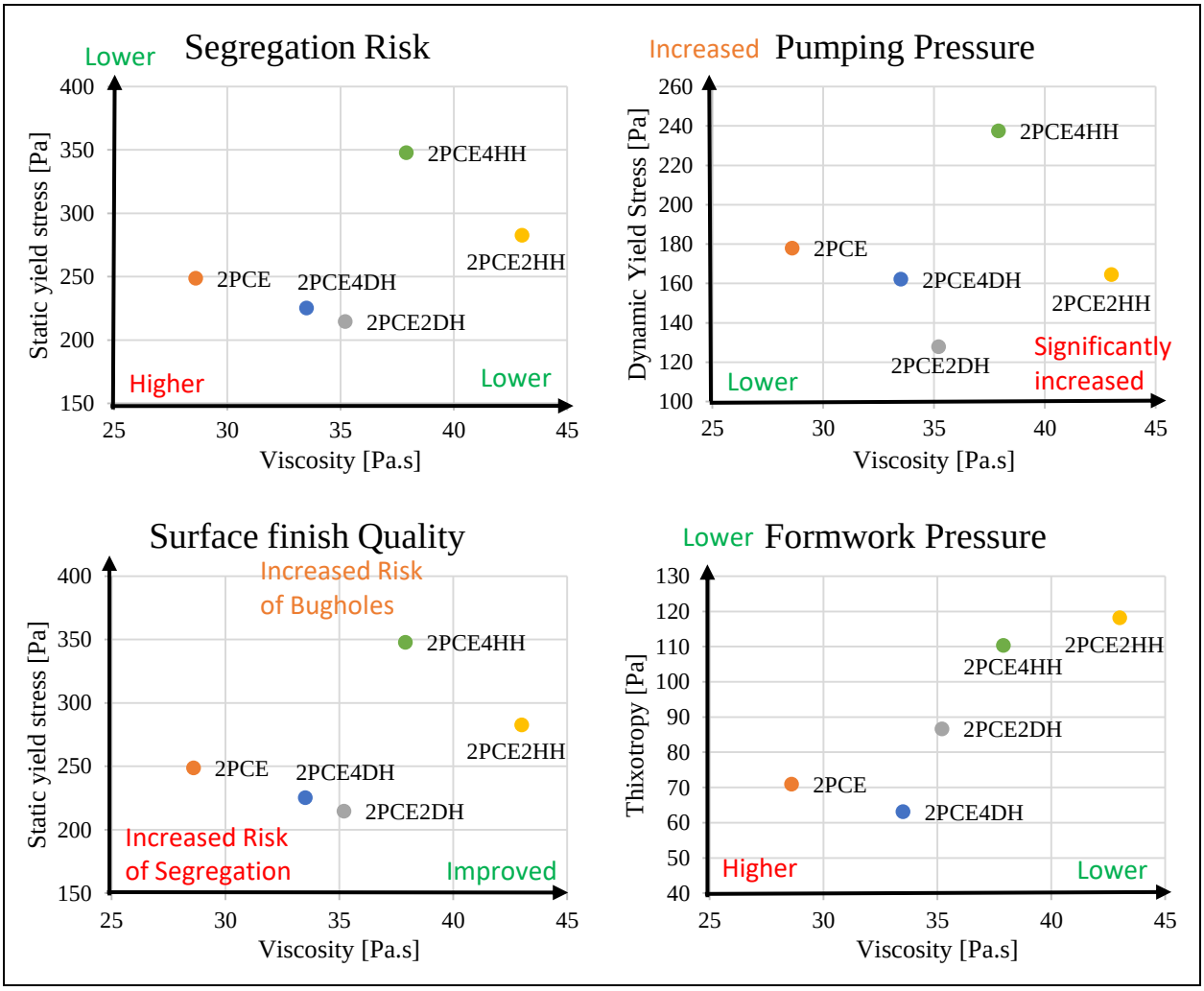


*Figure 4.17 Practical implication of PCE type superplasticiser – calcium sulphate interaction on concrete performance*

### 4.3.3.2 SNF type superplasticiser

The type of calcium sulphate present in cement also showed to influence the performance of SNF type superplasticiser. A significant difference in fresh state properties was observed between mixes containing dihydrate and hemihydrate, as presented in Figure 4.18.

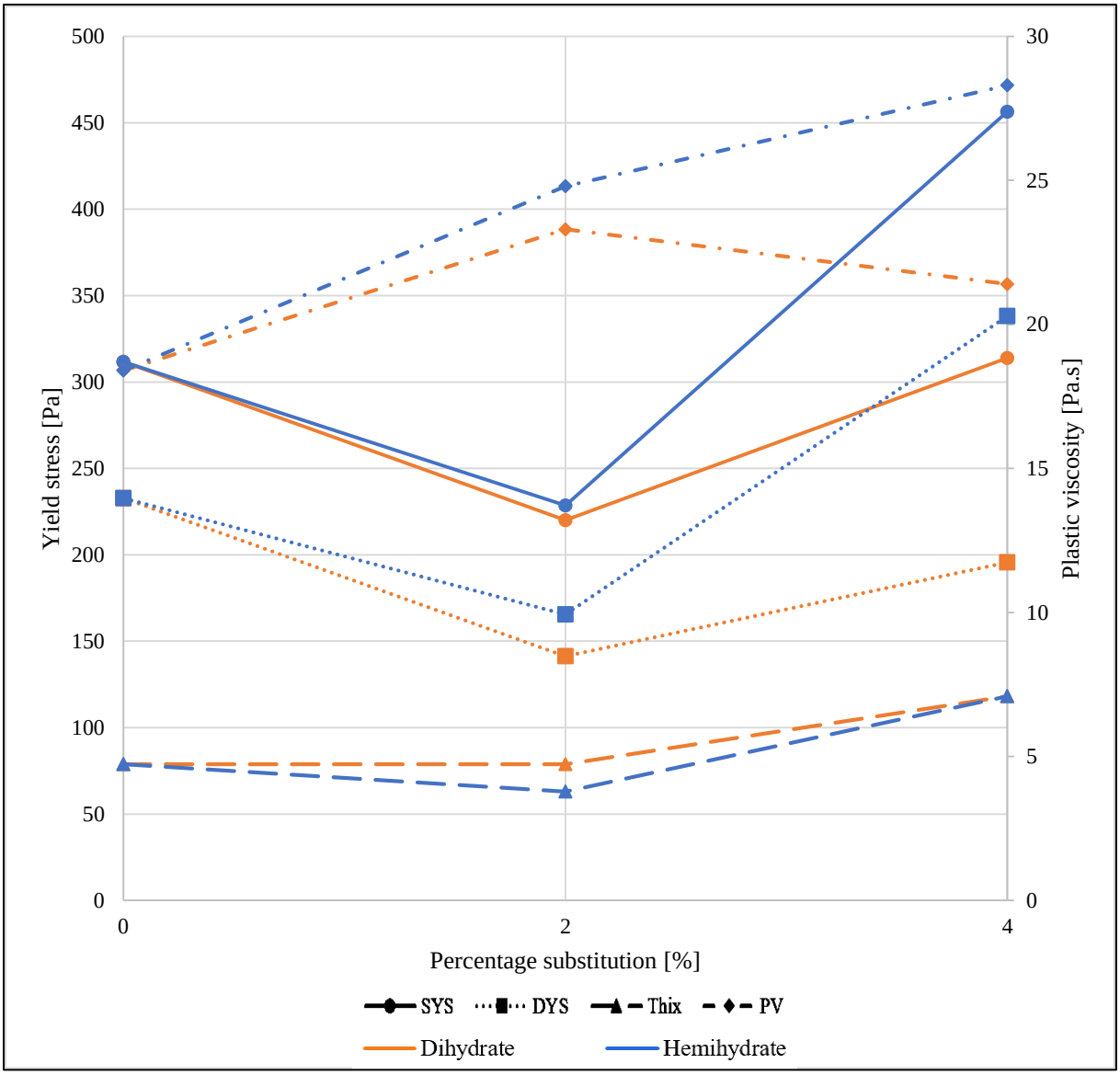


*Figure 4.18 Influence of SNF type superplasticiser – calcium sulphate interaction on initial fresh state properties*

The presence of dihydrate increased the slump flow of mixes containing SNF type superplasticiser, the increase in slump flow decreasing with the increase in dihydrate dosage. Hemihydrate also caused an increase in slump, however, slump increased with an increase in hemihydrate dosage. At 2% substitution with calcium sulphate, a decrease in SYS was observed, corresponding with the increase in slump. On the other hand, an increase in SYS was measured at 4% substitution, contradicting the increase in slump measured. This could indicate a slight delay in the dissolution of calcium sulphate in the presence of SNF type superplasticiser as a few minutes elapse between the slump flow and first Stress Growth (SG) tests; the reaction of dissolved sulphate with

tricalcium aluminates being responsible for the initial structuration of concrete in the fresh state. This delay could be more significant at lower dosages of calcium sulphate, hence the SYS still being lower than that measured in mix 2SNF during the first Stress Growth test. This would also explain the jump in SYS in mix 2SNF2HH at the 20 min mark while measuring the rate of structuration. No jump in SYS is observed in mix 2SNF2DH and 2SNF4DH as the dissolution rate is far lower than that of hemihydrate. Furthermore, it was found that the type of calcium sulphate showed no impact on the thixotropy of concrete containing SNF type superplasticiser. The presence of hemihydrate caused a significant increase in plastic viscosity, the plastic viscosity increasing with an increase in hemihydrate dosage. Although not evident in the initial setting time, which increased to more than 390 min for all mixes that contained SNF type superplasticiser and calcium sulphate substitutions, the presence of hemihydrate had a significant influence on the rate of structuration as shown in Figure 4.19.

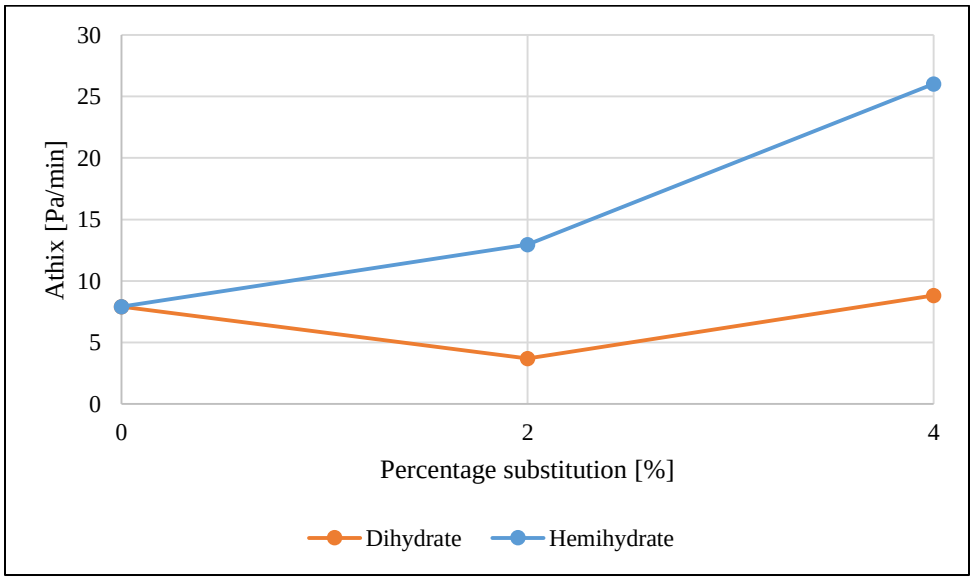


*Figure 4.19 Influence of SNF type superplasticiser – calcium sulphate interaction on the structuration rate of concrete*

A noteworthy increase in the rate of structuration was observed when SNF type superplasticiser was used in conjunction with cement containing hemihydrate as a source of calcium sulphate, this increase in the rate of structuration increasing significantly with an increase in hemihydrate dosage. It is reasoned that this is because of SNF type superplasticiser hindering the dissolution of calcium sulphates by forming a diffusion barrier at the liquid-solid interface through an increase in the sulphate concentration within the concrete solution. However, hemihydrate has a faster dissolution rate than dihydrate causing the concentration of sulphates at the solid-liquid interface

to quickly exceed that of the mix and continue diffusing throughout (Prince, Espagne and Aïtcin, 2003). This would allow for the continued formation of ettringite as sulphate ions diffuse throughout the mix solution and react with tricalcium aluminates. The development of a matrix of interlocked ettringite needles results in the structuration/stiffening of concrete within the fresh state.

The presence of hemihydrate reduces the ability of SNF type superplasticisers to induce fluidity. Furthermore, accelerated structuration is observed when SNF type superplasticiser is used with a cement containing hemihydrate. The implications on practical application of concrete with SNF type superplasticiser and which contains hemihydrate is as presented in Figure 4.20. Figure 4.20 shows that using hemihydrate as a source of calcium sulphate reduces the risk of segregation of concrete containing SNF type superplasticiser due to an increase in viscosity. However, this results in an increase in pumping pressures. Furthermore, a decrease in formwork pressure and increase surface finish quality occurs when hemihydrate is used as a source of calcium sulphate in concrete containing SNF type superplasticiser. However, the risk of bugholes on the concrete surface increases with high quantities of hemihydrate present in cement.

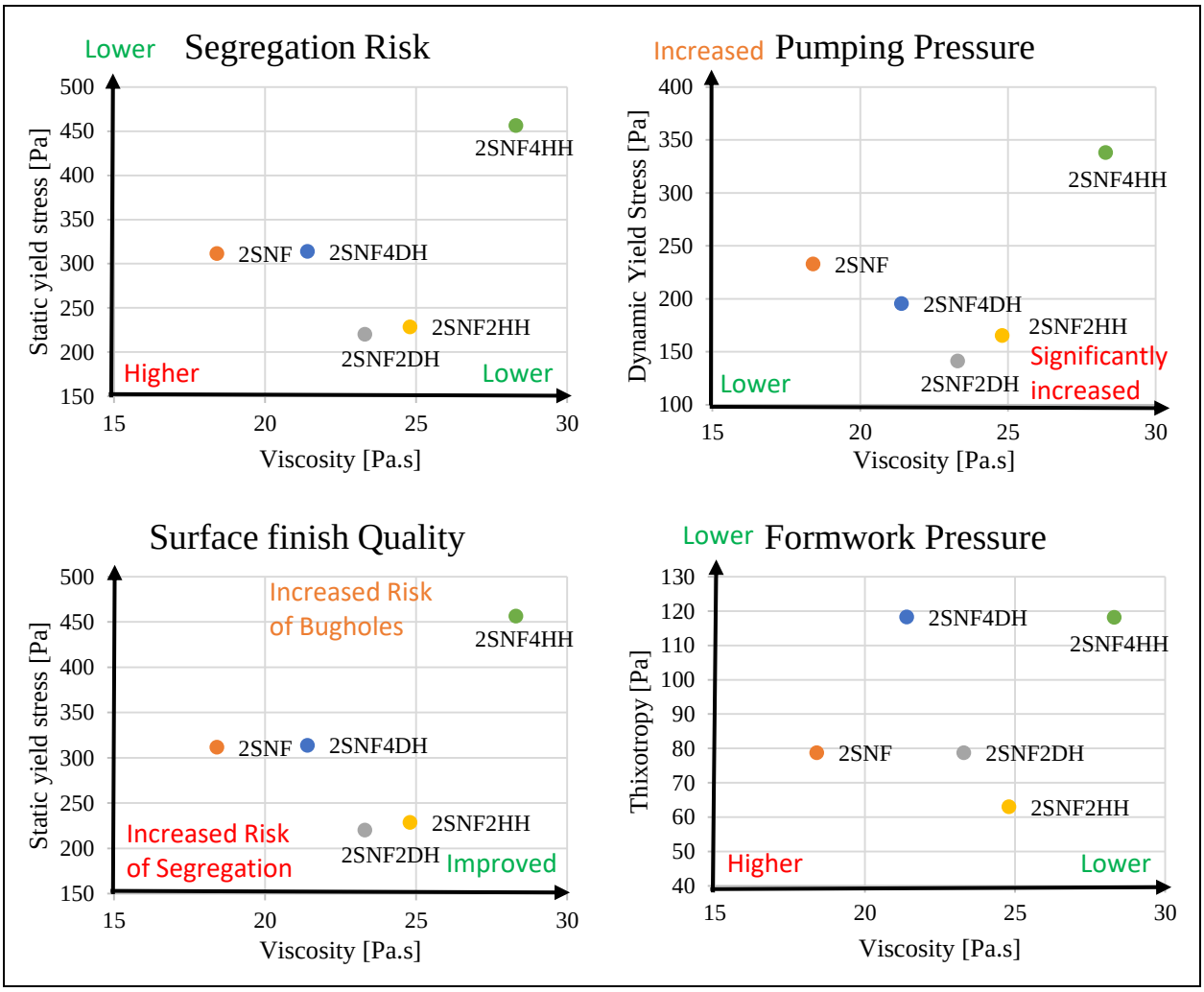


*Figure 4.20 Practical implication of SNF type superplasticiser – calcium sulphate interaction on concrete performance*

### 4.3.3.3 LS type plasticiser

From the results obtained, presented in Figure 4.21, it is clear that the behaviour of the LS type plasticiser is strongly dependent on the type of calcium sulphate present in cement.

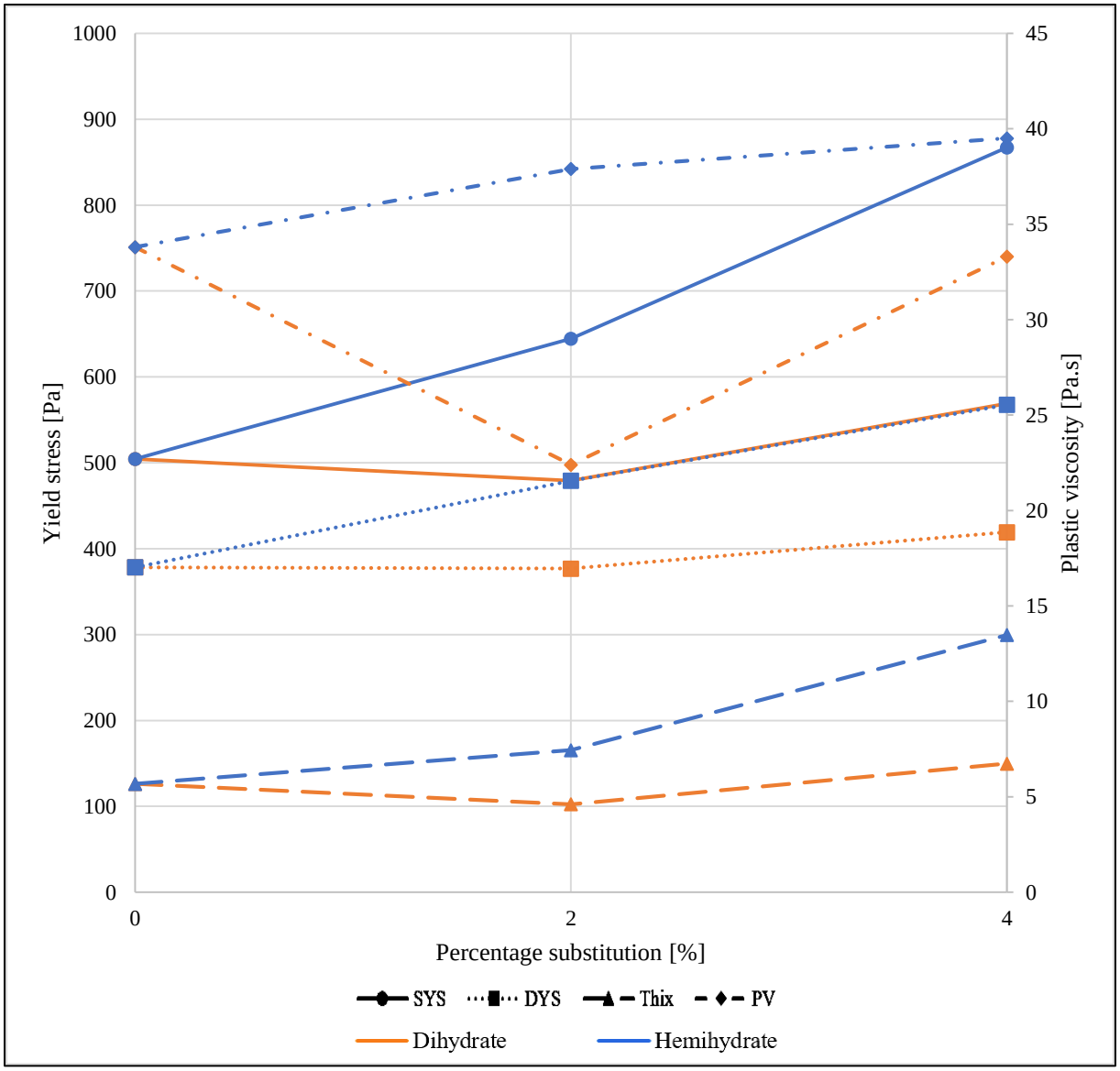


*Figure 4.21 Influence of LS type plasticiser – calcium sulphate interaction on initial fresh state properties*

The presence of hemihydrate caused a greater reduction in slump than dihydrate. This indicates that the presence of hemihydrate increases the water consumption of a mix when LS type plasticiser is present. This behaviour being more severe the higher the percentage of hemihydrate present within the cement. It is also observed that the SYS of mixes 2LS2HH and 2LS4HH is much higher than that of mix 2LS, therefore indicating that the presence of hemihydrate in cement completely eliminates the ability of LS type plasticiser to increase fluidity at the dosage used. This is substantiated by the significant decrease in slump of mixes containing hemihydrate. This can be explained by considering the influence of LS type plasticiser on the solubility of dihydrate and

hemihydrate respectively (as presented in Section 4.1). LS type plasticiser increases the solubility of hemihydrate considerably, while having a negligible effect on the solubility of dihydrate. This increase in hemihydrate solubility increases the water consumption of concrete. The presence of hemihydrate also caused the thixotropy and viscosity of the mix to increase significantly, this being more prominent the higher the percentage of hemihydrate present. The influence of hemihydrate on the performance of LS type plasticiser showed similar results to that of SNF type superplasticiser w.r.t the rate of structuration. The period for which fluidity is maintained is strongly influenced by the type of calcium sulphate present within cement as illustrated in Figure 4.22.

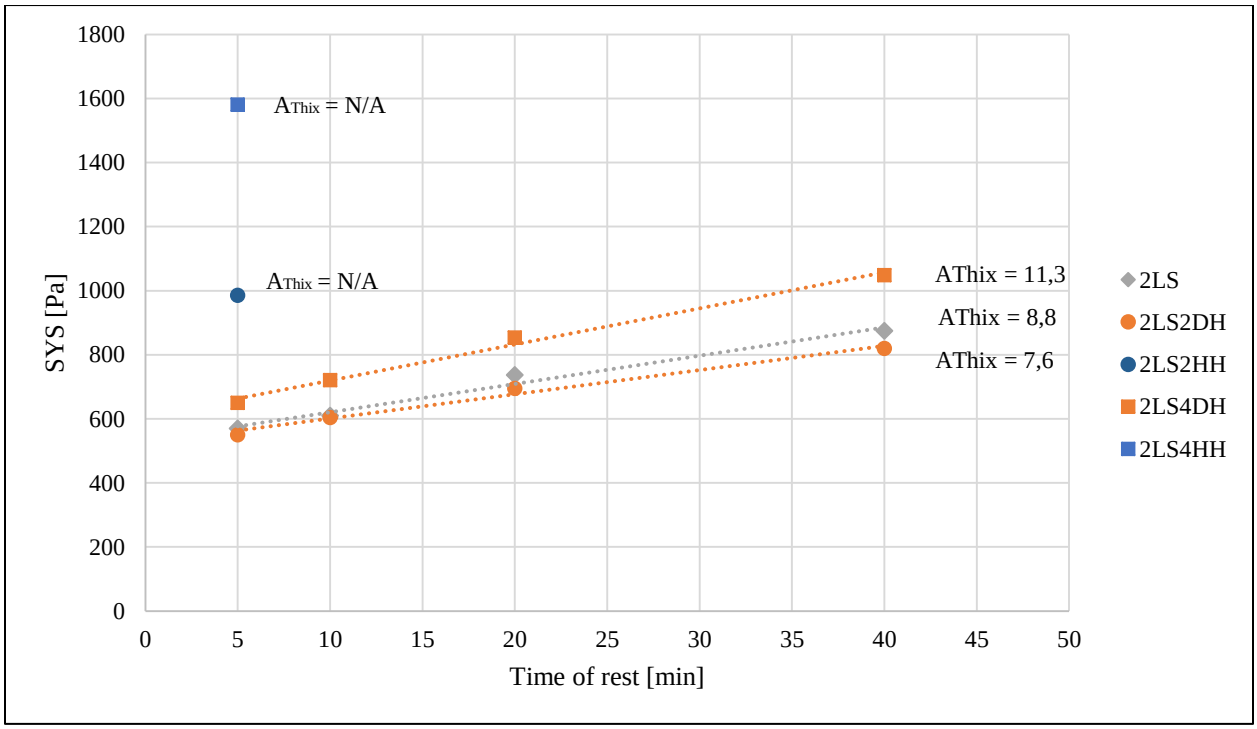


*Figure 4.22 Influence of LS type plasticiser – calcium sulphate interaction on the structuration rate of concrete*

Mixes 2LS2DH and 2LS4DH showed a slight, respective, decrease and increase in rate of structuration. On the other hand, mixes containing hemihydrate i.e. 2LS2HH and 2LS4HH experienced false set. This rapid stiffening resulted in both concrete mixes to shear around the ICAR Rheometer vane during testing causing the mix to shear non-homogeneously and a rate of structuration could not be obtained. It is predicted that this is caused by the increased solubility of hemihydrate in the presence of LS type superplasticiser resulting in false set. Initial setting times

of mixes 2LS2HH and 2LS4HH also showed a significant reduction when compared to those of 2LS2DH and 2LS4DH, irrespective of the dosage.

The influence of the interaction between LS type plasticiser and calcium sulphate on some practical applications are depicted in Figure 4.22. From this it can be seen that the presence of hemihydrate instead of dihydrate, as source of calcium sulphate in cement, improves the surface finish quality at lower quantities. However, at higher quantities of hemihydrate a significant increase in SYS is observed which, in conjunction with the increased PV, could result to air entrapment causing bugholes on the concrete surface. The risk of segregation of concrete containing LS type plasticiser is reduced when hemihydrate is present. Furthermore, formwork pressures are reduced while pumping pressure is increased for concrete containing LS type plasticiser when hemihydrate is present in cement.

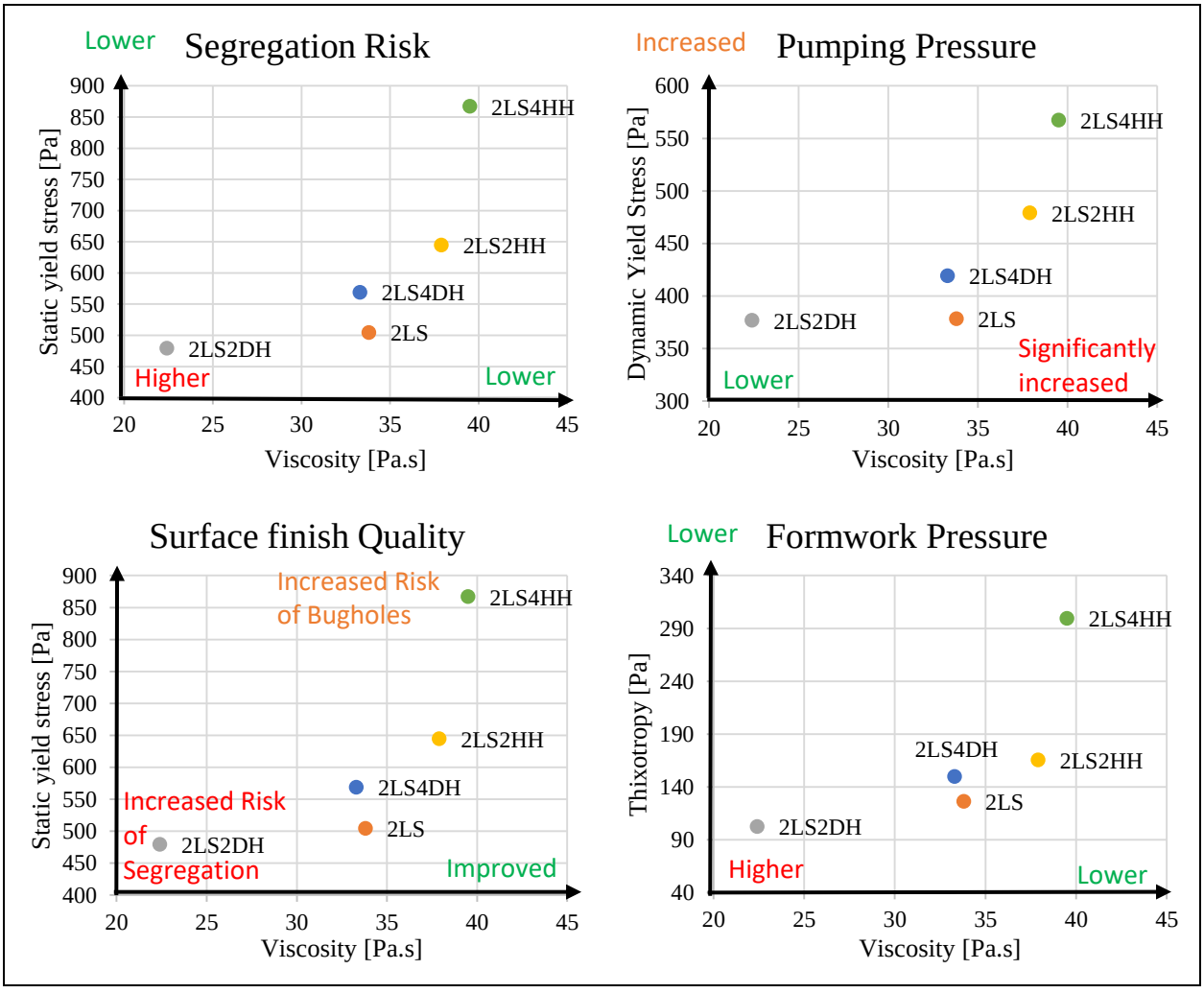


*Figure 4.23 Practical implication of LS type superplasticiser – calcium sulphate interaction on concrete performance*

## 4.4 Hardened state properties: compression strength

Strength gain in the hardened state, in terms of cube compression strength, of mixes containing various dosages of calcium sulphate, with different chemical nature, in conjunction with variable dosages of different forms of plasticiser/superplasticiser are presented in Table 4.4. The compression stress of all samples was normalized with respect to the reference mix's compression strength. This is done to ease the identification of delayed or accelerated strength gain.

*Table 4.4 Averaged cube compressive strength*

| | **Averaged compression strength [MPa]** | | | **Normalised average compression strength [kN]** | | |
|---|---|---|---|---|---|---|
| | **1 day** | **3 day** | **7 day** | **1 day** | **3 day** | **7 day** |
| **REF** | 22,1 | 33,5 | 41,0 | 1,00 | 1,00 | 1,00 |
| **2DH** | 21,0 | 35,5 | 37,5 | 0,95 | 1,06 | 0,92 |
| **4DH** | 22,2 | 34,6 | 41,2 | 1,02 | 1,00 | 1,01 |
| **2HH** | 22,0 | 35,6 | 40,0 | 1,04 | 1,03 | 0,98 |
| **4HH** | 26,3 | 38,8 | 44,2 | 1,19 | 1,14 | 1,09 |
| **PCE** | 23,2 | 33,9 | 43,4 | 1,09 | 0,98 | 1,05 |
| **2PCE** | 24,8 | 39,8 | 42,7 | 1,17 | 1,17 | 1,01 |
| **2PCE2DH** | 18,1 | 32,5 | 38,6 | 0,82 | 0,93 | 0,96 |
| **2PCE2HH** | 21,5 | 38,2 | 43,8 | 0,97 | 1,13 | 1,07 |
| **2PCE4DH** | 25,1 | 42,1 | 46,1 | 1,18 | 1,27 | 1,12 |
| **2PCE4HH** | 25,3 | 43,4 | 47,3 | 1,15 | 1,26 | 1,14 |
| **SNF** | 20,2 | 32,7 | 38,4 | 0,93 | 0,92 | 0,91 |
| **2SNF** | 14,5 | 33,6 | 42,1 | 0,68 | 1,00 | 1,06 |
| **2SNF2DH** | 4,2 | 35,1 | 41,2 | 0,19 | 1,04 | 1,01 |
| **2SNF2HH** | 12,7 | 36,9 | 42,1 | 0,56 | 1,05 | 1,02 |
| **2SNF4DH** | 4,8 | 39,2 | 42,3 | 0,21 | 1,11 | 1,01 |
| **2SNF4HH** | 16,0 | 40,9 | 46,2 | 0,78 | 1,17 | 1,12 |
| **LS** | 21,4 | 36,7 | 39,6 | 1,04 | 1,08 | 0,96 |
| **2LS** | 19,7 | 34,0 | 39,4 | 0,84 | 0,99 | 0,98 |
| **2LS2DH** | 18,3 | 31,5 | 37,6 | 0,79 | 0,94 | 0,93 |
| **2LS2HH** | 18,1 | 34,7 | 39,3 | 0,83 | 1,03 | 0,98 |
| **2LS4DH** | 19,6 | 34,8 | 40,1 | 0,94 | 0,99 | 0,98 |
| **2LS4HH** | 21,8 | 37,1 | 41,1 | 0,98 | 1,11 | 1,01 |

### 4.4.1 Calcium sulphate

From the results (Figure 4.24) obtained it is evident that the type of calcium sulphate present in cement influences the strength gain of concrete. The figure shows that the presence of hemihydrate in cement accelerates strength gain. This is seen in the respective 19% 1 day and 14% 3 day compressive strength increase of mixes substituted with 4% hemihydrate. These results concurs with those reported by Gunay *et al.* (2011). The study of Gunay *et al.* (2011) found that the early strength gain of concrete increases with the increase of calcium sulphate. This is due to the influence of calcium sulphate on $C_3S$ hydration. With elevated quantities of dissolved sulphates within the concrete solution the S/Ca ratio in CSH products increases. This phenomena modifies CSH morphology, therefore changing the permeability of $C_3S$ grains and hydration kinetics. It is found that quantity of calcium sulphate required to regulate $C_3A$ hydration is often lower than the quantity that leads to optimum initial CSH growth i.e. initial strength gain (Gunay *et al.*, 2011; Zunino and Scrivener, 2019). It is postulated that the lower compressive strength of mixes substituted with dihydrate and 2% hemihydrate is due to the calcium sulphate not contributing to strength gain at the same magnitude as the calcium silicates that were removed during substitution. Furthermore, it can be seen that the period over and magnitude with which strength gain is accelerated, increases with an increase in dosage of hemihydrate. On the other hand, the addition of dihydrate had negligible effect on the rate of strength gain of concrete and showed a lower compression strength than mixes containing hemihydrate at all ages and dosages. This might be an indication that the onset of CSH development occurs at an earlier concrete age when hemihydrate is present i.e. when the solubility of calcium sulphate present in cement is increased, as CSH development is the primary cause for strength gain in cementitious materials. This is supported by the results obtained in Section 4.2. From the tests conducted in Section 4.2 it was found that the presence of hemihydrate, in comparison with dihydrate, causes a reduction in "dormant period". This would indicate that hemihydrate causes earlier onset of CSH development.

The accelerated early strength gain caused by the presence of hemihydrate in cementitious materials could present various advantages during construction. One such advantage is a reduction of concrete curing periods. Structural concrete is usually cured for a period required to build up 70% of the specified compressive strength (ACI 301-16, 2002). The period before the removal of formwork is also shortened seeing that structural elements will be able to withstand own weight and construction loads at an earlier concrete age, making formwork available for reuse.

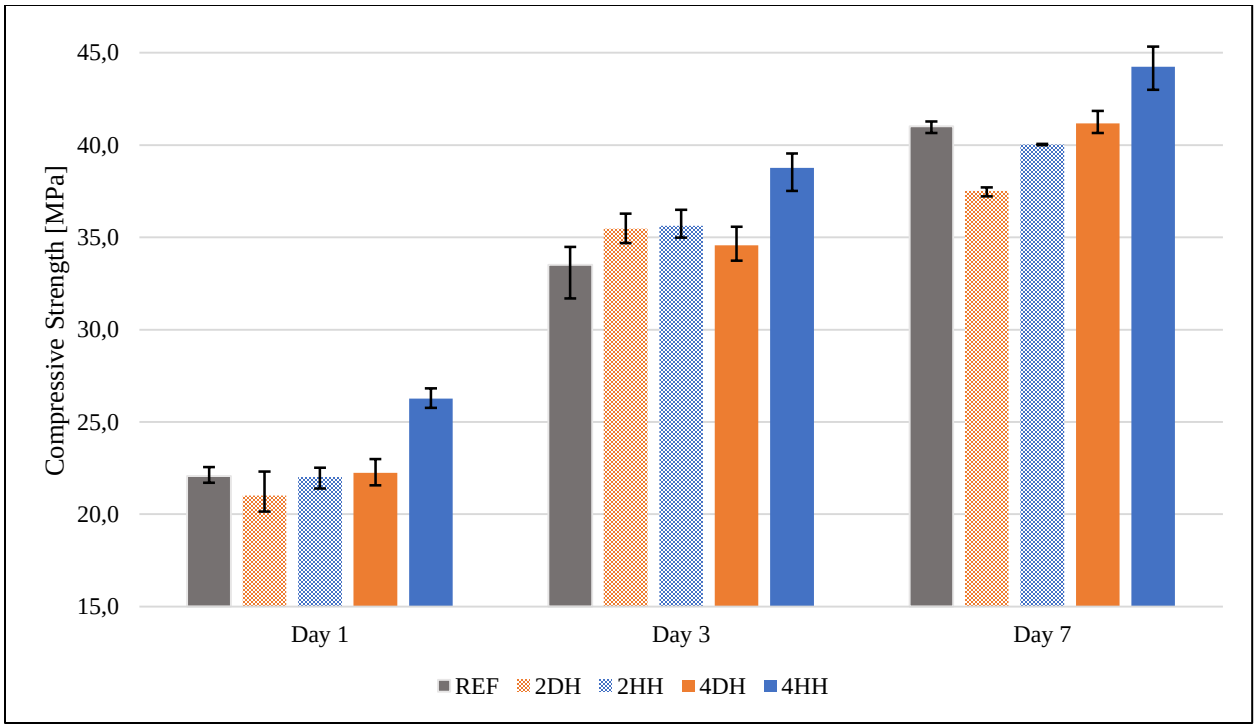


*Figure 4.24 Influence of the type of calcium sulphate on mechanical strength gain*

## 4.4.2 Plasticiser/superplasticiser

Plasticiser/superplasticiser also influenced the rate of strength gain in the hardened state as presented in Figure 4.25. However, this influence is dependent on the type of plasticiser/superplasticiser used. PCE type superplasticiser caused an overall increase in strength gain, this becoming less prominent at older concrete ages. This increase in concrete strength is more significant at higher dosages of PCE type superplasticisers. SNF type superplasticiser, on the other hand, caused a significant decrease in the initial rate of strength gain as seen by the decrease in 1 day compression strength. This delay in initial strength gain increased significantly with an increase in SNF type superplasticiser dosage. However, at 3 day age the delay in strength gain dissipates and a slight increase in rate of strength gain is observed at higher SNF type superplasticiser dosages. LS type plasticiser exhibited similar behaviour as SNF type superplasticiser, however, the delay in initial strength gain was less severe. Furthermore, at higher dosages of LS type plasticiser the delay in strength gain continued up to 7 day age.

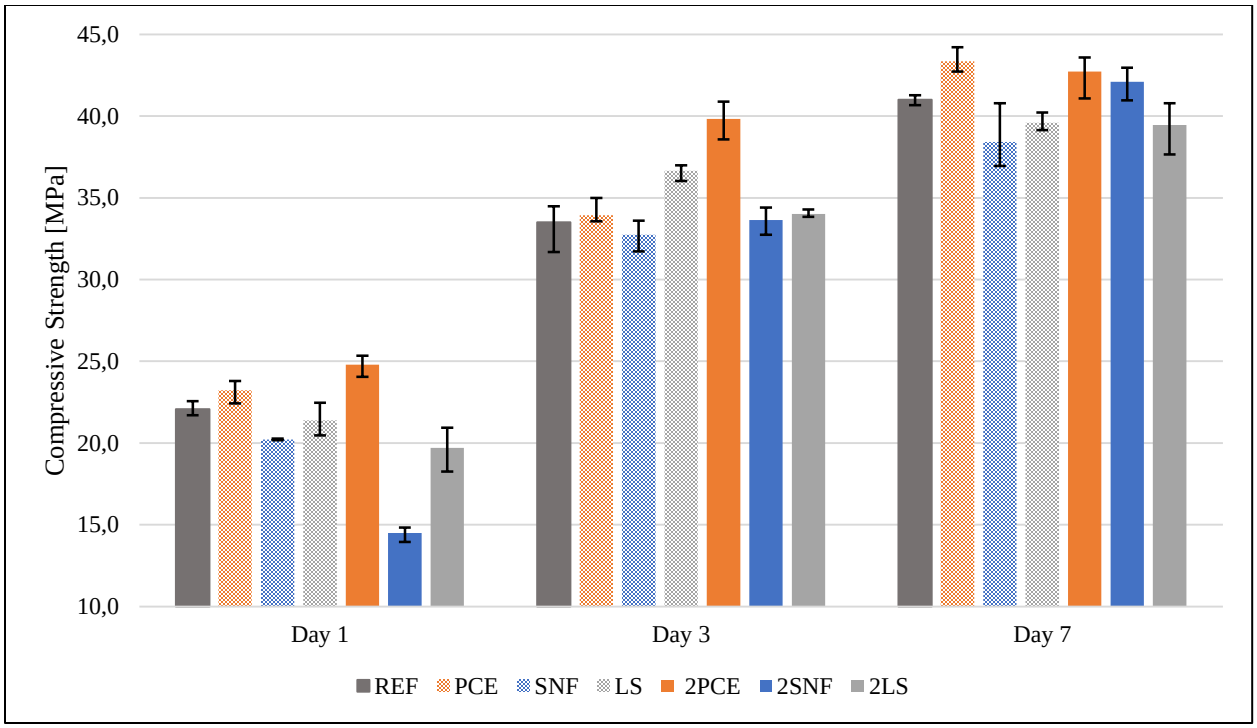


*Figure 4.25 Influence of plasticiser/superplasticiser on mechanical strength gain*

## 4.4.3 Calcium sulphate – plasticiser/superplasticiser interaction

Although the respective influence of calcium sulphate and plasticiser/superplasticiser on the strength gain of concrete is well documented, the influence of the interaction between calcium sulphate and plasticiser/superplasticiser is still undetermined. The influence of the calcium sulphate to superplasticiser interaction on the strength gain of concrete is therefore quantified in this section.

### 4.4.3.1 PCE type superplasticiser

The rate of strength gain is dependent on both the nature and dosage of calcium sulphate used. At lower dosages, a significant difference was observed between mixes containing dihydrate and hemihydrate, mixes containing hemihydrate always presenting higher compression strength. Although both dihydrate and hemihydrate showed a decrease in the rate of strength gain at 2% substitution, this decrease was less severe in the case of hemihydrate. The influence of the type of calcium sulphate used on strength gain is negligible at higher dosages of calcium sulphate substitution. Furthermore, an increase in the rate of strength gain is observed at 4% calcium sulphate substitution, irrespective of the type of calcium sulphate.

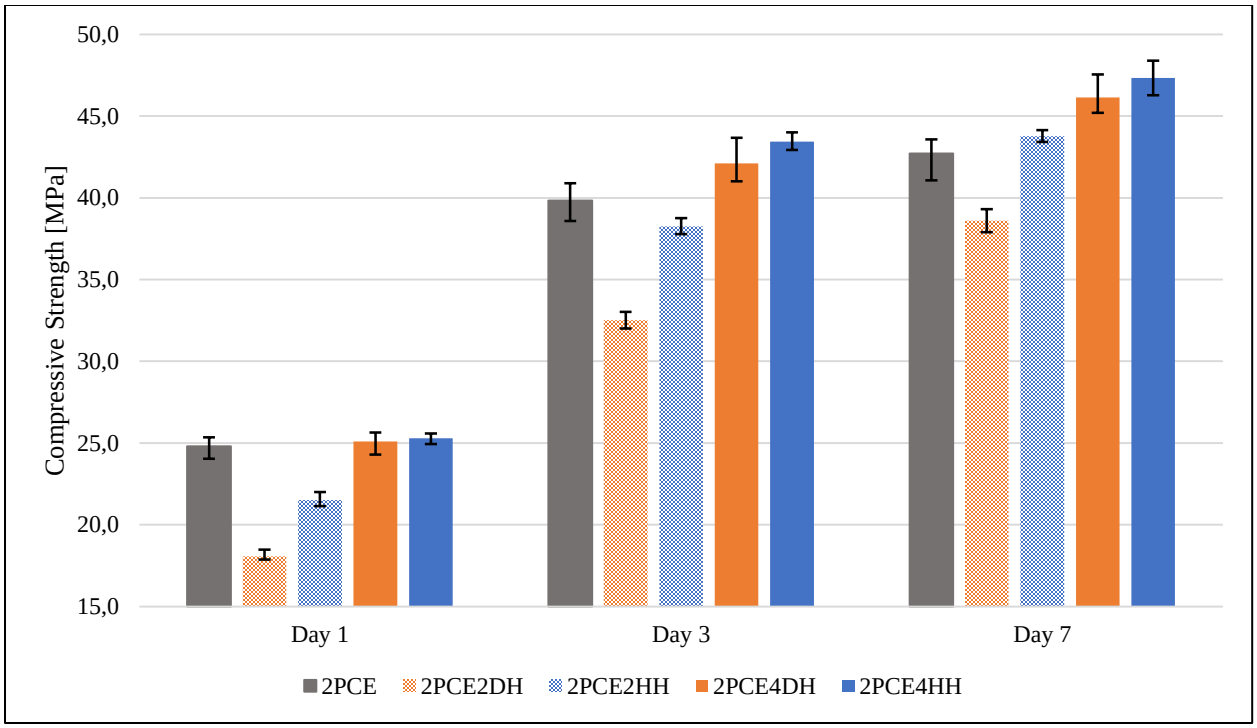


*Figure 4.26 Influence of PCE type superplasticiser – calcium sulphate interaction on mechanical strength gain*

#### 4.4.3.2 SNF type superplasticiser

The initial strength gain of concrete containing SNF type superplasticiser is strongly dependent on the type of calcium sulphate present in cement as seen in Figure 2.13. All concrete mixes that were modified through the partial substitution of dihydrate showed a reduction in initial strength gain. The significant decrease in 1 day compressive strength of mixes containing SNF type superplasticiser and substituted with dihydrate could be as a result in the excessive increase in 'dormant period' as presented in Figure 4.6, the 'dormant period' of mix 2SNF4DH being extended to more than 17 hours. On the other hand substitution with 4% hemihydrate showed a slight increase in initial rate of strength gain in the hardened state. At 3 day and 7 day concrete age the strength was increased through the addition of calcium sulphate, irrespective of the nature. This increase in strength was more prominent the higher the substitution with calcium sulphate. However, this increase in strength was always more significant when hemihydrate was present. This could be due to the increased solubility of hemihydrate increasing the quantity of dissolved sulphate available which alters CSH growth as described in Section 4.4.1.

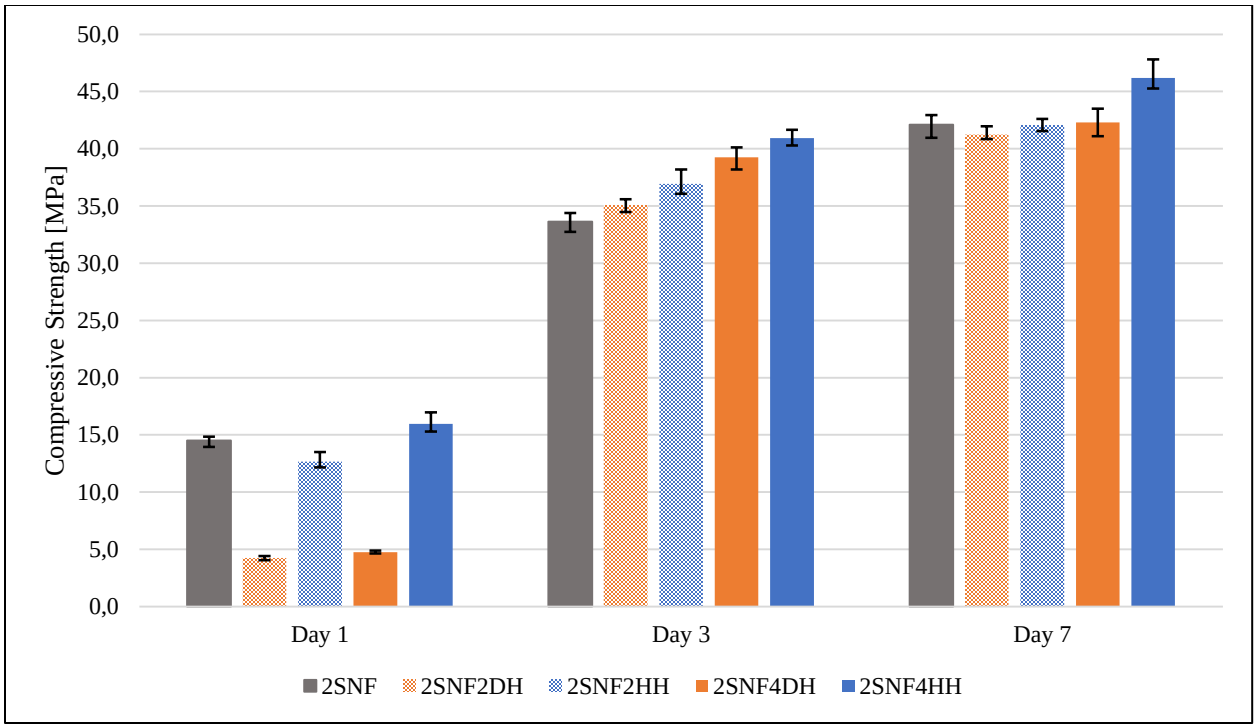


*Figure 4.27 Influence of SNF type superplasticiser – calcium sulphate interaction on mechanical strength gain*

### 4.4.3.3 LS type plasticiser

The presence of hemihydrate caused an increase in the rate of strength gain in concrete mixes containing LS type plasticiser, compared to those containing dihydrate as seen in Figure 4.28. At 4% substitution of hemihydrate, the delayed strength gain associated with the use of LS type plasticiser was completely counteracted at all concrete ages. At 4% substitution with dihydrate, an increase in strength was also observed, however, the extent thereof was not as significant. This could once again be attributed to the respective solubilities / rate of dissolution of dihydrate and hemihydrate as a high levels in dissolved sulphate promote CSH growth.

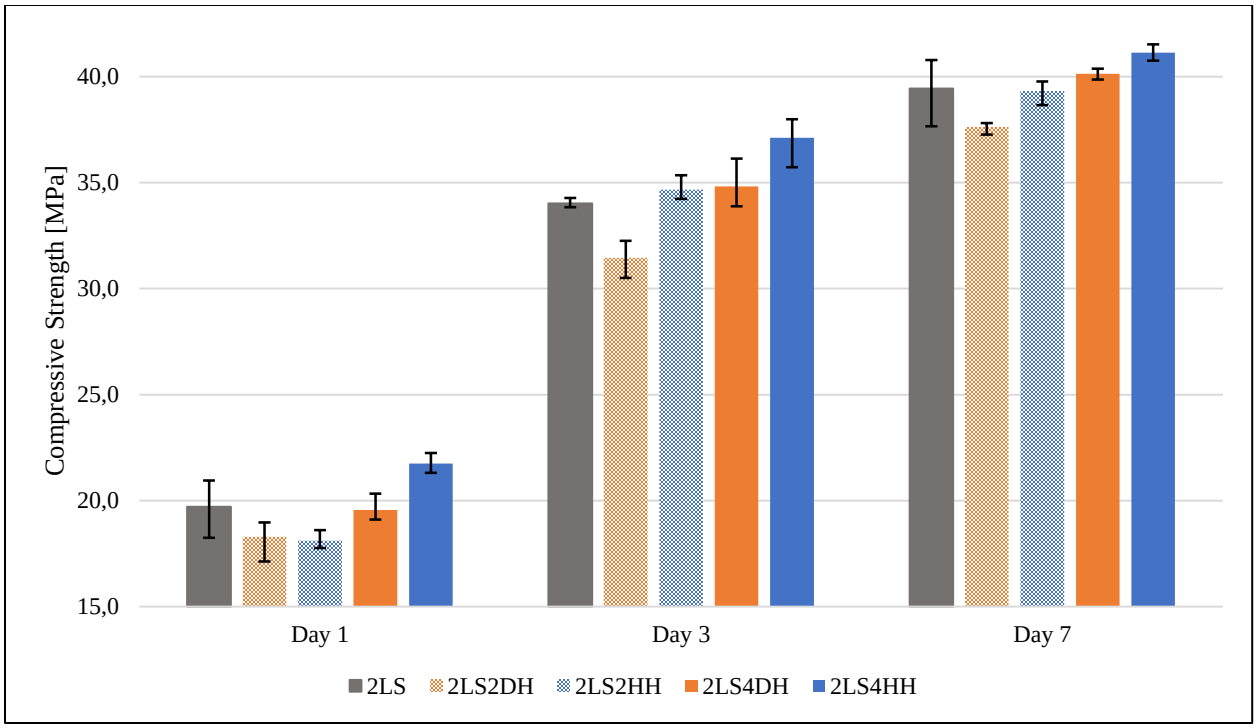


*Figure 4.28 Influence of LS type plasticiser – calcium sulphate interaction on mechanical strength gain*

# Chapter 5: Conclusions

From the tests conducted in this study the flowing significant conclusions can be drawn with regard to the influence of the relation between calcium sulphate and plasticiser/superplasticiser on concrete performance:

- The nature of the calcium sulphate in cement influences both initial fresh state properties and hydration of concrete. Hemihydrate increases the water demand as well as the hydration rate of cementitious materials. Hemihydrate therefore decreases the initial fluidity of concrete while increasing the rate at which concrete stiffens in the fresh state. This is undesirable for concrete that has to maintain workability over long periods, for example, SCC or ready mix concrete that's transported over long distances. However, the use of hemihydrate, as a source of calcium sulphate, can be beneficial for applications were rapid stiffening of concrete is required as is the case for 3D printed concrete or the casting of deep concrete sections were formwork pressures are a problem. Furthermore, it is observed that hemihydrate increases the rate of strength gain in the hardened state of concrete, this being more prominent at higher dosages of hemihydrate. This is as a result of hemihydrate reducing the length of the dormant period during hydration. It is anticipated that this is an indication that the onset of CSH development occurs at an earlier concrete age when hemihydrate is present i.e. when the solubility of calcium sulphate present in cement is increased, as CSH development is the primary cause for strength gain in cementitious materials. The accelerated initial compressive strength gain of cementitious materials containing hemihydrate could be beneficial to construction as it would reduce the curing period of structural concrete and the period that formwork is required.
- Plasticiser/superplasticiser are often incorporated into a mix design to increase fluidity while maintaining a constant w/c ratio. However, these chemical admixtures can increase the risk of segregation and delayed hydration. Although prolonging the period for which fluidity is maintained may be beneficial as it extends the time that concrete can be worked, it can also delay construction productivity. This is because of high formwork pressure, as a result of delayed strength gain in the fresh state, limiting the casting height. The influence of the plasticiser/superplasticiser on strength gain in the hardened state is dependent on the type of superplasticiser used. The PCE type superplasticiser caused a significant increase in concrete

workability without causing a delay in compressive strength gain. The SNF type superplasticiser on the other hand increased concrete workability but also caused a delay in compressive strength gain; the 1 day compressive strength of concrete containing SNF type superplasticiser being considerably lower than that of the reference mix. The LS type plasticiser also showed to be a sufficient liquidising agent, but did delay compressive strength gain at high dosages.

- When the influence of the type of calcium sulphate on the performance of PCE type superplasticiser is examined it is found that the presence of hemihydrate significantly reduces the initial fluidity induced by the PCE type superplasticisers. This is unfavourable when PCE type superplasticiser is used as a fluidising agent in conjunction with cement that contains hemihydrate. However, it is found that the nature of the calcium sulphate present in cement does not influence the rate at which concrete stiffens, the dosage, on the other hand, having a significant influence on the rate of structuration. While the form of the calcium sulphate does not influence the period that fluidity is maintained of concrete containing PCE type superplasticiser, it is evident that PCE type superplasticiser is sensitive to the quantity of sulphate available in the concrete solution. It is observed that the amount of calcium sulphate in concrete also influences the strength gain of concrete containing PCE type superplasticiser. The compressive strength of concrete mixes that were substituted with 4% calcium sulphate were considerably higher than those substituted with 2% calcium sulphate. Furthermore, it can be concluded that the hydration kinetics is not influenced significantly by the type of calcium sulphate in cement.
- The efficiency of SNF type superplasticiser also showed sensitivity to the type of calcium sulphate. Although the presence of hemihydrate caused a slight reduction in initial slump compared to mixes substituted with dihydrate, the workability of concrete was improved with the substitution of calcium sulphate irrespective of the type of calcium sulphate used. SNF type superplasticiser therefore maintain their efficiency as a fluidising agent when hemihydrate is present in cement. However, the period for which fluidity is maintained is significantly reduced when hemihydrate is present in cement as it causes accelerated structuration i.e. stiffening of mixes containing SNF type superplasticiser. Hemihydrate, as a source of calcium sulphate thus counters the delayed hydration associated with SNF type superplasticiser without reducing the initial workability. This could be both beneficial and disadvantageous depending on the

application of the mix design. The accelerated structuration could speed up construction as the concrete will build strength faster in the fresh state, resulting in reduced formwork pressures which allows for the casting of deeper sections in one pour. However, SNF type superplasticiser is predominately used in ready mix concrete for its ability to delay hydration, allowing time for transfer. Accelerated concrete mix stiffening, as is caused by the presence of hemihydrate in cement, would therefore be unwanted. Furthermore, it is observed that hemihydrate accelerates the initial strength gain of concrete containing SNF type superplasticiser. It is observed that the presence of hemihydrate significantly reduces the dormant period of mixes containing SNF type superplasticiser, resulting in earlier strength gain.

- The performance of LS type plasticiser is significantly dominated by the type of calcium sulphate present in cement. The presence of hemihydrate, in place of dihydrate, eliminates the ability of LS type plasticiser to induce fluidity. Irrespective of the dosage of hemihydrate used, a significant increase in initial stiffness was observed. Furthermore, after 10 min of resting time, the mix exhibited false set which did not occur in any mixes that did not contain LS type plasticiser. It can, therefore, be concluded that LS type plasticisers are extremely sensitive to the type of calcium sulphate present in cement. Hemihydrate also causes an increase in early age strength gain of concrete containing LS type plasticiser. This could be as a result of hemihydrate accelerating the rate of hydration.

It can be concluded that the temperature at which clinker and dihydrate is milled together, to produce cement, should be carefully monitored as high milling temperatures would result in the dehydration of dihydrate to hemihydrate, and to a lesser extent anhydrite. From this study it is seen that the type of calcium sulphate present in cement influence the both the fresh and hardened state properties of concrete. Furthermore, the calcium sulphate to plasticiser/superplasticiser relation, and the influence thereof on the performance of concrete, is unique to each calcium sulphate and chemical admixture combination. Improper combinations could result in undesirable concrete performance.

# Chapter 6: Recommendations

To build on the results obtained in this study the following recommendations are made.

For this study, the influence of the relation between calcium sulphate and plasticiser/superplasticiser on the performance of concrete was evaluated through substituting the binder content of mixes with either dihydrate or hemihydrate. This increased the percentage of calcium sulphate in the binder to a maximum of 7.8%. However, it should be kept in mind that the upper limit for the calcium sulphate percentage allowed in OPC in accordance with SANS 50197-1:2013 is 5% (SANS, 2013). Furthermore, the percentage of calcium sulphate, in cement, that is made up of dihydrate and hemihydrate before substitution is unknown. It is therefore recommended that clinker should be milled and the desired quantity of dihydrate and/or hemihydrate added afterwards and homogenised. For this study it was opted to use a CEM I, supplied by PPC (Pretoria Portland Cement Co. Ltd.), due the difficulty of obtaining raw clinker in the volume required. The milling of the clinker to the desired fineness and under the correct conditions would also presented difficulty.

The environmental temperature would also influence the calcium sulphate to plasticiser/superplasticiser interaction. This is due to the solubility of calcium sulphate being temperature sensitive. Further studies should thus be conducted to determine the influence of the calcium sulphate to plasticiser/superplasticiser interaction in locations of extreme temperatures.

Furthermore, various forms of chemically diverse plasticisers/superplasticisers exist. This is specifically true for PCE type superplasticiser. The relationship between calcium sulphate and a range of chemically diverse PCE type superplasticisers should therefore be considered to draw a conclusion on how this relationship influences the performance of concrete. The addition time of plasticiser/superplasticiser will also influence the calcium sulphate to plasticiser/superplasticiser interaction. If plasticiser/superplasticiser addition time is delayed, calcium sulphate will have sufficient time to dissolve and react with the aluminate phase which could alter the calcium sulphate to plasticiser/superplasticiser interaction.

Moreover, a wide range of diverse chemical and mineral admixtures exists that are incorporated into modern concrete design to obtain desired concrete performance. The use of these admixtures in conjunction with each other could lead to compatibility issues and cause unwanted concrete

performance. Research should thus be conducted to understand the interaction between admixtures that are often used in conjunction with each other for example SCM and plasticiser/superplasticisers.

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